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Radical Reduction of Aromatic Azides to Amines with Triethylsilane

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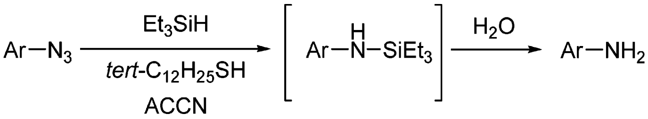
Received April 19, 2006



Aromatic azides are inert toward triethylsilane under thermal conditions in the presence of a radical initiator, but in the presence of additional catalytic amounts of *tert*-dodecanethiol, they afford anilinosilanes and thence the corresponding anilines in virtually quantitative yields.

Since the discovery of organic azides more than a century ago, numerous syntheses of these energy-rich molecules have been exploited and their applications in organic synthesis have enormously widened.[1] Radical reactions of azides are still less documented, but the reported studies have clearly revealed that these reactions also provide useful synthetic routes to N-heterocycles.[2,3]

Straightforward reduction to amines is one of the most attractive synthetic applications of azides. Since aliphatic azides are readily available from the corresponding halides and sulfonates, they serve as one of the most reliable ways to introduce an amino substituent onto an aliphatic carbon. The conversion of aromatic azides into anilines has received relatively modest interest until very recently, especially since those azides have been mostly produced from the anilines themselves via their diazonium salts.[1,4,5] Nowadays, an easy entry to anilines from aryl azides has become highly appealing due to the recent finding that aryl azides can be generally produced in very good yields upon CuI-catalyzed coupling reaction of the corresponding iodides and bromides with sodium azide under mild thermal conditions.[6]

The conversion of azides to amines can be achieved by a large variety of reported methods.[1,7] The procedure involving tributyltin hydride (Bu_3SnH) in the presence of a radical initiator (AIBN) has found almost invariable use to perform that process under radical conditions.[8,9] Incidentally, the *N*-stannylaminyl radicals involved in this process can alternatively act as key intermediates in numerous interesting azide cyclization/rearrangement processes mediated by Bu_3SnH/AIBN.[8,10] This method is unfortunately limited by the known toxicity of organotin compounds and, additionally, the serious problems connected with full removal of tin residues from the reaction mixtures. Therefore, replacement of Bu_3SnH with other nontoxic group XIV hydrides, such as the organosilicon or organogermanium ones, is highly desirable. On this basis, in a very recent work, we have made first successful use of a triorganogermanium hydride (Bu_3GeH) in the radical aryl azides reduction.[11] To circumvent the poor hydrogen-donating properties of the germanium hydride, the procedure has been carried out following the "polarity reversal catalysis" technique introduced by Roberts[12] and upgraded by Bowman,[13] that is, by using Bu_3GeH in the presence of catalytic benzenethiol in refluxing toluene (Scheme 1, Y = Ph, X = Bu_3Ge).[14] Our tin-free radical

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(1) (a) *The Chemistry of the Azido Group*; Patai, S., Ed.; Wiley: New York, 1971. (b) *Azides and Nitrenes: Reactivity and Utility*; Scriven, E. F. V., Ed.; Academic Press: New York, 1984. (c) Scriven, E. F. V.; Turnbull, R. *Chem. Rev.* **1988**, *88*, 297. (d) Bräse, S.; Gil, C.; Knepper, K.; Zimmermann, V. *Angew. Chem., Int. Ed.* **2005**, *44*, 5188.

(2) For selected reactions of carbon-centered radicals with alkyl and aryl azides, see: (a) Benati, L.; Montevecchi, P. C.; Spagnolo, P. *Tetrahedron Lett.* **1978**, 815. (b) Benati, L.; Montevecchi, P. C. *J. Org. Chem.* **1981**, *46*, 4570. (c) Kim, S.; Joe, G. H.; Do, J. Y. *J. Am. Chem. Soc.* **1994**, *116*, 5521. (d) Montevecchi, P. C.; Navacchia, M. L.; Spagnolo, P. *Eur. J. Org. Chem.* **1998**, 1219. (e) Benati, L.; Leardini, R.; Minozzi, M.; Nanni, D.; Spagnolo, P.; Strazzari, S.; Zanardi, G. *Org. Lett.* **2002**, *4*, 3079. (f) Lizos, D. E.; Murphy, J. A. *Org. Biomol. Chem.* **2003**, *1*, 117.

(3) For recent examples of radical azidations using sulfonyl azides, see: (a) Renaud, P.; Ollivier, C. *J. Am. Chem. Soc.* **2001**, *123*, 4717. (b) Renaud, P.; Ollivier, C.; Panchaud, P. *Angew. Chem., Int. Ed.* **2002**, *41*, 3460. (c) Renaud, P.; Ollivier, C.; Panchaud, P.; Zigmantas, S. *J. Org. Chem.* **2004**, *69*, 2755.

(4) Liu, Q.; Tor, Y. *Org. Lett.* **2003**, *5*, 2571 and references cited therein.

(5) Rodriguez, J. A. R.; Abramovitch, R. A.; de Souse, J. D. F.; Leiva, G. C. *J. Org. Chem.* **2004**, *69*, 2920.

(6) (a) Feldman, A. K.; Colasson, B.; Fokin, V. V. *Org. Lett.* **2004**, *6*, 2571. (b) Zhu, W.; Ma, D. *Chem. Commun.* **2004**, 888. (c) Cai, Q.; Zhu, W.; Zhang, Y.; Ma, D. *Synthesis* **2005**, 498. (d) Andersen, J.; Madsen, U.; Bjorkling, F.; Liang, X. *Synlett* **2005**, 2209. (e) Andersen, J.; Bolvig, S.; Liang, X. *Synlett* **2005**, 2941.

(7) For a comprehensive review on azide reduction methods, see: Amantini, D.; Fringuelli, F.; Pizzo, F.; Vaccaro, L. *Org. Prep. Proc. Int.* **2002**, *34*, 109.

(8) (a) Kim, S.; Joe, G. H.; Do, J. Y. *J. Am. Chem. Soc.* **1993**, *115*, 3328. (b) Kim, S.; Kim, S. S.; Seo, H. S.; Yoon, K. S. *Tetrahedron* **1995**, *51*, 8437. (c) Dang, H.-S.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 1* **1996**, 1493. (d) Benati, L.; Bencivenni, G.; Leardini, R.; Minozzi, M.; Nanni, D.; Scialpi, R.; Spagnolo, P.; Zanardi, G. *J. Org. Chem.* **2005**, *70*, 3046.

(9) (a) Frankel, M.; Wagner, D.; Gertner, D.; Zikha, A. *J. Organomet. Chem.* **1967**, *7*, 518. (b) Samano, M. C.; Robins, M. J. *Tetrahedron Lett.* **1991**, *32*, 6293. (c) Poopeiko, N. E.; Pricota, T. I.; Mikhailopulo, I. A. *Synlett* **1991**, 342. (d) Hornemann, A. M.; Lundt, I. *J. Org. Chem.* **1998**, *63*, 1919. (e) Hays, D. S.; Fu, G. C. *J. Org. Chem.* **1998**, *63*, 2796. (f) Benati, L.; Leardini, R.; Minozzi, M.; Nanni, D.; Spagnolo, P.; Strazzari, S.; Zanardi, G. *Tetrahedron* **2002**, *58*, 3485. (g) Zaitseva, V. E.; Dyatkina, N. B.; Kraevskii, A. A.; Skaptsova, N. V.; Turina, O. V.; Gottikh, B. P.; Azhaev, A. V. *Bioorg. Khim. (Moscow)* **1984**, *10*, 670; *Chem. Abstr.* **1984**, *101*, 192378c.

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(11) Benati, L.; Bencivenni, G.; Leardini, R.; Minozzi, M.; Nanni, D.; Scialpi, R.; Spagnolo, P.; Zanardi, G. *J. Org. Chem.* **2006**, *71*, 434. Also a group XIII hydride, namely, dichloroindium hydride, has just been proved to react smoothly with organic azides: Benati, L.; Bencivenni, G.; Leardini, R.; Nanni, D.; Minozzi, M.; Spagnolo, P.; Scialpi, R.; Zanardi, G. *Org. Lett.* **2006**, *8*, 2499.

(12) (a) Roberts, B. P. *Chem. Soc. Rev.* **1999**, *28*, 25. (b) Dang, H.-S.; Roberts, B. P.; Tocher, D. A. *J. Chem. Soc., Perkin Trans. 1* **2001**, 2452. (c) Cai, Y.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **2002**, 1858.

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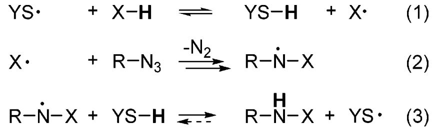
10.1021/jo060824k CCC: $33.50

SCHEME 1

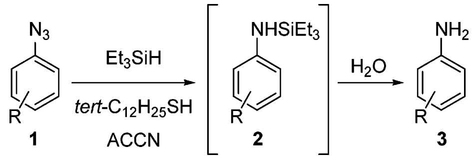


$$\mathrm{YS\cdot} + \mathrm{X{-}H} \rightleftharpoons \mathrm{YS{-}H} + \mathrm{X\cdot} \qquad (1)$$

$$\mathrm{X\cdot} + \mathrm{R{-}N_3} \xrightarrow{-N_2} \mathrm{R{-}\dot{N}{-}X} \qquad (2)$$

$$\mathrm{R{-}\dot{N}{-}X} + \mathrm{YS{-}H} \rightleftharpoons \mathrm{R{-}\overset{H}{N}{-}X} + \mathrm{YS\cdot} \qquad (3)$$

TABLE 1. Reduction of Aromatic Azides 1 to Amines 3[a]



entry	azide	R	amine (% yield)[b]
1	**1a**	4-OMe	**3a** (>98) [98]
2	**1b**	4-Me	**3b** (>98)
3	**1c**	4-H	**3c** (>98)
4	**1d**	4-CN	**3d** (>98) [98]
5	**1e**	4-F	**3e** (>98)
6	**1f**	4-Cl	**3f** (>98) [98]
7	**1g**	4-Br	**3g** (- -)[c]
8	**1h**	4-I	**3h** (- -)[c]
9	**1i**	4-COMe	**3i** (80)[d]
10	**1j**	4-COOMe	**3j** (>98)
11	**1k**	4-COOH	**3k** (>98)
12	**1l**	4-NO_2	**3l** (30)[e]
13	**1m**	3-OMe	**3m** (>98)
14	**1n**	3-Cl	**3n** (>98)
15	**1o**	2-OMe	**3o** (>98)
16	**1p**	2-Me	**3p** (>98)
17	**1q**	2-Ph	**3q** (>98)
18	**1r**	2-F	**3r** (>98)
19	**1s**	2-Cl	**3s** (>98)
20	**1t**[f]		**3t** (>98)
21	**1u**[g]		**3u** (>98)

[a] Reactions were normally carried out in a toluene (3 mL) solution containing azide **1** (0.5 mmol), Et_3SiH (2 mmol), ACCN (0.075 mmol), and *tert*-dodecanethiol (0.075 mmol) at 110 °C for 4 h. [b] Yields estimated by ^1H NMR spectroscopy; yields in square brackets are for the pure products isolated by column chromatography. [c] Unchanged starting azide (**1g** or **1h**) and small amounts of phenyl azide (**1c**) were only obtained. [d] Unchanged azide **1i** was also obtained in 18% yield. [e] Unchanged azide **1l** was also obtained in70% yield. [f] **1t**: 1-naphthyl azide. [g] **1u**: 2-naphthyl azide.

protocol suffered, however, from limitations arising from use of the rather costly germanium hydride as well as concomitant production of significant amounts of 2-germylated anilines as side products.

A consequential extension of the above study was to examine the possibility of carrying out analogous radical azide reductions by employing an alternative group XIV reagent, such as triethylsilane (Et_3SiH), which is a stable, safe, and cheap compound. The synthetic potential of radical azide reactions with silyl hydrides is virtually unexplored, although as early as 1979 triorganosilyl radicals derived from silanes, including triethylsilane, have been reported to react with phenyl azide and various alkyl azides to give rise to EPR spectra ascribable to silyltriazenyl adducts.[15] To our knowledge, there are only two reported examples of radical (alkynyl) azide reaction with a silane: in those cases, the reduced amines were actually produced in moderate yields by using a rather peculiar (and expensive) silane, namely, tris(trimethylsilyl)silane.[2d,16]

Preliminary experiments revealed that in refluxing toluene several aryl azides remained virtually unaffected upon treatment with up to 4-fold excess of Et_3SiH in the presence of a radical initiator, such as ACCN (1,1′-azobiscyclohexane-1-carbonitrile). Triethylsilane alone, similar to Bu_3GeH,[11,14] seemed therefore unable to reduce aryl azides under radical conditions; this fact was presumably due to inhibition of the chain reaction caused by inefficient H-transfer[17] from the (nucleophilic) silane to the derived *N*-silylaminyl radicals, which, like the *N*-stannyl and *N*-germyl analogues,[11,18] are predicted to have nucleophilic properties, as well.

We then decided to extend the polarity reversal catalysis technique to the present silane reactions by using *tert*-dodecanethiol as a catalyst.[19] Interestingly, in the presence of ACCN (0.15 equiv) and catalytic *tert*-dodecanethiol (0.15 equiv), 4-methoxyphenyl azide **1a** (0.5 mmol) was totally consumed by Et_3SiH (2 equiv) in a degassed toluene (3 mL) solution kept in a sealed tube at 110 °C for ca. 4 h. Direct GC−MS analysis of the resultant reaction mixture showed the almost exclusive presence of 4-methoxy-*N*-(trimethylsilyl)aniline **2a** and, to a small extent, 4-methoxyaniline **3a**. After evaporation of the excess reagent and solvent under vacuum, the ^1H NMR spectrum of the crude residue in $CDCl_3$ solution revealed the virtually quantitative presence of the sole aniline **3a** owing to presumably hydrolytic removal of the precursor **2a**. Subsequent column chromatography isolated aniline **3a** in nearly quantitative yield (98%) (Table 1, entry 1).

In light of this successful result, we were prompted to examine analogous reactions of other aryl azides, including the *ortho*-, *meta*-, and *para*-substituted phenyl azides **1b**−**s** as well as 1- and 2-naphthyl azides **1t**,**u**, which are all shown in Table 1. Since we next discovered that certain aryl azides, unlike the congener **1a**, failed to undergo entire consumption using a 2-fold excess of Et_3SiH, all the subsequent reduction reactions were carried out with a larger excess of the silane reagent (4 equiv).[20] In the presence of a 4-fold excess of the silane, the *para*-substituted azides **1b**−**f**,**j**,**k** behaved in a fashion strictly comparable to that of **1a**, furnishing virtually quantitative yields of the corresponding anilines **3b**−**f**,**j**,**k**, as established by ^1H NMR analysis of the crude residues arising from concentration of the respective reaction mixture (Table 1, entries 2−6, 10, 11). The *meta*- and *ortho*-substituted phenyl azides **1m**−**s**, as well as the naphthyl azides **1t**,**u**, also led to the corresponding anilines **3m**−**u** in practically quantitative yields, as similarly shown by ^1H NMR analysis (Table 1, entries 13−21). In two cases (**1d** and **1f**), chromatographic purification of the crude product allowed nearly quantitative isolation of the pure anilines **3d**,**f** (Table 1, entries 4 and 6).[21]

The corresponding reactions of 4-azidoacetophenone **1i** and 4-nitrophenyl azide **1l** were instead (somewhat) less rewarding.

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(14) Indeed, in the absence of benzenethiol, aryl azides remained completely unaffected by the Bu_3GeH/ACCN system.

(15) (a) Roberts, B. P.; Winter, J. N. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1353. (b) Brand, J. C.; Roberts, B. P.; Winter, J. N. *J. Chem. Soc., Perkin Trans. 2* **1983**, 261.

(16) Tris(trimethylsilyl)silane, though being an expensive compound, has often replaced Bu_3SnH to mediate radical chain processes due to comparable strength of the Si−H bond.

(17) Triethylsilane is expected to be a less effective H-donor than Bu_3GeH due to significantly stronger Si−H bond.

(18) Kim, S.; Yeon, K. M.; Yoon, K. S. *Tetrahedron Lett.* **1997**, *38*, 3919.

(19) Several arene- and alkanethiols, including thiophenol, triphenylsilanethiol, methyl thioglycolate, and *n*-undecanethiol, were evaluated as possible catalysts, but the best results were obtained with *tert*-dodecanethiol, which is, by the way, the cheapest and least malodorous thiol. Alkanethiols, and especially the tertiary ones, are known to play a crucial catalytic role in promoting radical chain reductions of alkyl halides, which involve nucleophilic carbon radical intermediates unable to abstract hydrogen from triorganosilanes; see ref 12.

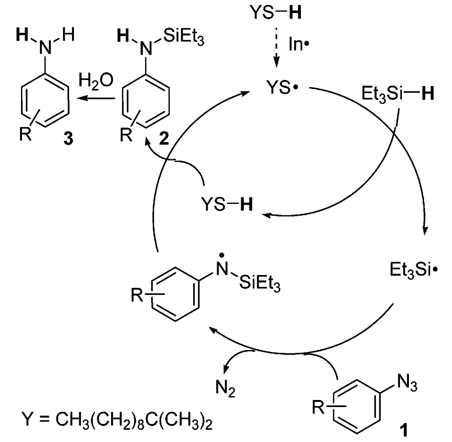
The former, though unusually affording a significant amount of unreacted azide (18%), still furnished a good yield of (4-aminophenyl)ethanone **3i** (80%), whereas the latter preferentially gave a much unaltered substrate (70%) with only a modest amount of 4-nitroaniline **3l** (30%) (Table 1, entries 9 and 12). However, the poor reaction of azide **1l** was not unexpected in view of the known fact that the nitro group can act as an efficient scavenger of radical species and can thus interfere with radical propagation cycles.[11]

Finally, our reactions with 4-bromo- (**1g**) and 4-iodophenyl azide (**1h**) revealed an essential inertness of these two azides with triethylsilane. Indeed, both reactions, while totally failing to furnish the usual amine, gave back the unchanged azide accompanied by small amounts of dehalogenated phenyl azide (**1c**) (Table 1, entries 7 and 8).

A radical mechanism for our present reactions was clearly supported by the general fact that, in the absence of ACCN initiator, the aromatic azides **1** remained totally unaffected by Et_3SiH/*tert*-dodecanethiol under the usual thermal conditions. We therefore suggest that an initially formed *tert*-dodecanesulfanyl radical abstracts hydrogen from Et_3SiH, yielding a triethylsilyl radical. This radical adds to the aromatic azido group to give an *N*-silylarylaminyl radical presumably through loss of nitrogen by a transient 1,3- or 3,3-silyltriazenyl radical adduct.[11,15] Eventual reduction of the silylarylaminyl radical by *tert*-dodecanethiol affords *N*-silylaniline **2** with concomitant regeneration of the *tert*-dodecanesulfanyl radical (Scheme 2).

N-Silylanilines **2** evidently were the hydrolytic precursors of the final anilines **3**. In fact, in all of the examined cases, GC−MS analysis of the resulting reaction mixtures, as just obtained at the end of the reaction, disclosed that silanes **2** rather than anilines **3** were the primary, often almost exclusive components. Further spectral substantiation was generally prevented by the inherent propensity of compounds **2** to suffer hydrolytic conversion into anilines **3** even upon simple concentration of the original reaction mixtures. However, with 4-methoxyphenyl azide **1a**, spectral support for the primary intervention of silylaniline **2a** was successfully achieved by ^1H and ^{13}C NMR analysis of the reaction mixture obtained from the reduction of **1a** carried out in $C_6D_5CD_3$ solution.

SCHEME 2



It is worth noting that concrete evidence for analogous intervention of initial *N*-stannyl- and/or *N*-germyl amines in corresponding radical azide reductions with Bu_3SnH and Bu_3GeH is to date essentially missing.[8,9,11] Anilinosilanes are known to be useful intermediates in synthetic processes;[22] our present findings interestingly suggest that the radical silane reaction with aromatic azides might, in principle, offer an attractive means for the generation and in situ exploitation of those compounds.

As far as the observed inertness of the 4-halophenyl azides **1g**,**h** with our silane, this might be explained in terms of initial occurrence of bromo- and iodotriethylsilane as a result of preferred halogen abstraction by the triethylsilyl radical. Silyl radicals derived from tris(trimethylsilyl)silane are known to achieve halogen abstraction from aliphatic bromo- and iodoazides in preference to addition to the azido moiety,[2c,e] but no data for the behavior of silyl radicals with the aromatic haloazides are available. Further reaction of the produced halosilane with the nucleophilic dodecanethiol would cause consumption of the catalyst, thence causing substantial inhibition of the radical chain reductive process that might afford the (observed) dehalogenated phenyl azide (**1c**). Similar reasons have been reported to explain the known reluctance of alkyl bromides and iodides to undergo thiol-catalyzed reductions with silanes.[12c,23]

In the present work, we also performed a brief investigation of the radical silane reaction with aliphatic azides. Under the standard conditions, 3-phenylpropyl azide **4a** afforded the amine **6a** in 40% yield, with ca. 55% of the azide recovered unreacted in the absence of any significant trace of other side products. Under more forcing conditions (10-fold excess of Et_3SiH), the yield of **6a** was considerably enhanced (75%), but azide **4a** still remained unchanged to a noticeable extent (ca. 20%) (Scheme 3). Undecyl azide **4b** and 4-cyanobutyl azide **4c** were even less rewarding since, under the more forcing conditions (10-fold

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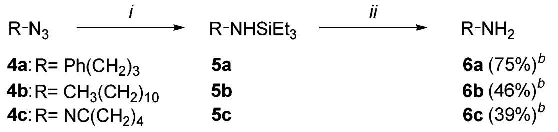
[20] Using a 2-fold excess of Et_3SiH, poorly electron-rich and, especially, electron-deficient aryl azides were often found to undergo reductive conversion not exceeding 80−90% over ca. 4 h; prolongation of the reaction time was usually ineffective. Presently, we do not have any conclusive explanation of the reason electron-poor aryl azides require a greater excess of silane to be totally converted into anilines. However, since silyl radicals are supposed to be nucleophilic, the addition step of those intermediates to the azido function should be faster with electron-deficient azides; this suggests that the step affecting the overall reaction outcome could be the second one, that is, the hydrogen abstraction process of the N-silylated nitrogen-centered radical from the thiol. Hydrogen transfers are known to be strongly affected by polar effects and charge separation in the transition state. See, for example: Feray, L.; Kuznetsov, N.; Renaud, P. In *Radicals in Organic Synthesis*; Renaud, P., Sibi, M. P., Eds.; Wiley-VCH: Weinheim, Germany, 2001: Vol. *2*, Chapter 3.6, pp 246−278. Therefore, it would not be unreasonable to assume that in azides **1** the ring substituent could stabilize or destabilize an incipient charge on the nitrogen atom of the intermediate silylaminyl radical. If the transition state requires H-transfer from an electrophilic ($\delta-$) sulfur atom to a nucleophilic ($\delta+$) aminyl radical, then an electron-donating group should be able to stabilize the electron deficiency on the nitrogen atom, thus favoring the hydrogen donation and the concomitant regeneration of the sulfanyl radical. If we suppose that reactions 1 and 3 of Scheme 1 ($Y = tert\text{-}C_{12}H_{25}$, $X = Et_3Si$) could be reversible, then increasing the amount of the silane would be a crucial point for favoring the trapping of the aminyl radical and thence the complete conversion of the starting material.

[21] Reactions were normally carried out on 0.5 mmol of azide **1**, but identical results can be obtained on a larger scale (e.g., 10 mmol).

[22] (a) Ando, W.; Tsumaky, H. *Synthesis* **1982**, 263. (b) Rajeswari, S.; Jones, R. J.; Cava, M. P. *Tetrahedron Lett.* **1987**, *28*, 5099. (c) El-Qurashi, M. A. M.; Ali, H. M. *Thermochim. Acta* **1997**, *293*, 185. (d) Iida, A.; Horii, A.; Misaki, T.; Tanabe, Y. *Synthesis* **2005**, 2677.

[23] The reported rate constants for halogen abstraction by triethylsilyl radicals from aryl halides at 383 K are as follows: 2.9×10^6 M^{-1} s^{-1} (ArCl), 7.7×10^8 M^{-1} s^{-1} (ArBr), and 6.7×10^9 M^{-1} s^{-1} (ArI). See: Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5123. Since in our hands 4-chlorophenyl azide **1f**, contrary to the halophenyl congeners **1g**,**h**, underwent exclusive reduction of the azido function in preference to dehalogenation, the rate constant for the addition of triethylsilyl radicals to an aromatic azido function might be predicted to be ca. 10^7 M^{-1} s^{-1}.

SCHEME 3[a]



[a] Reagents and conditions: *i*, Et_3SiH (10 equiv), ACCN (0.15 equiv), *tert*-dodecanethiol (0.15 equiv), toluene, 110 °C, 4 h; *ii*, H_2O. [b]Yields were estimated by ^{1}H NMR spectroscopy.

excess of silane), they gave only moderate yields of amines **6b**,**c**, giving back much more unaltered starting substrate (50−55%) (Scheme 3). Direct GC−MS analysis of the original reaction mixtures disclosed that also in these cases silylamines (**5a**−**c**) were the primary reduction products. The apparent reluctance of azides **4a**−**c** to suffer essential consumption with Et_3SiH is consistent with our own evidence that aliphatic azides are similarly less prone than the aromatic ones to undergo radical reduction with Bu_3GeH/PhSH.[24,25] However, the actual reasons for the markedly different behavior displayed by the aromatic and aliphatic azides toward the silane (and the germanium hydride) remain rather unclear at this stage. A clear knowledge of the actual role played by transient 1,3- and/or 3,3-silyl- (or germyl-) triazenyl radical adducts, which are the presumable precursors of the aminyl radicals, is totally lacking and, if available, it would probably throw a brighter light on this matter.[8d,11,26,27]

In conclusion, we have discovered a novel thiol-catalyzed radical chain reaction of triethylsilane with aromatic azides, which provides an appealing tin-free protocol for the reduction of those azides to amines. This protocol is clearly superior to the previous one using tributylgermanium hydride since, while using a simple and very cheap silane reagent, it provides clean aniline products in excellent yields. Additional interest arises from the finding that the radical silane reaction with aromatic azides smoothly affords anilinosilane precursors, which in principle might be exploited in situ for further synthetic processes.

Experimental Section

Reactions of Azides 1 with Triethylsilane: General Procedure. A toluene (3 mL) solution containing azide **1** (0.5 mmol) and ACCN (0.075 mmol, 0.15 equiv) was degassed under vacuum (15 Torr) in a Schlenk flask at 0 °C for 15 min, after which triethylsilane (2 mmol, 4 equiv) and *tert*-dodecanethiol (0.015 mmol, 0.15 equiv) were added under a nitrogen atmosphere. The flask was immediately sealed and then kept at 110 °C for 4 h. After cooling to room temperature, the resulting reaction mixture was directly analyzed by GC−MS to show the main presence of anilinosilane **2** accompanied by small amounts of aniline **3**. Subsequent removal of the excess reagent and solvent under reduced pressure gave a residue mostly containing aniline **3**. This was subjected to chromatographic purification on silica gel by gradual elution with light petroleum/diethyl ether mixtures, to give the pure aniline **3**, and/or analyzed by ^{1}H NMR spectroscopy in $CDCl_3$ solution.

Acknowledgment. The authors acknowledge financial support from MIUR (2004−2005 funds for “Free Radicals in Oxidation Reactions and in New Synthetic Processes”) and the University of Bologna.

Supporting Information Available: Preparation of aryl azides **1a**−**u** and alkyl azides **4a**−**c**; mass data of anilinosilanes **2a**−**u** and alkylaminosilanes **5a**−**c**, and NMR data of **2a**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO060824K

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[24] In sharp contrast with aromatic azides, under comparable and/or more forcing conditions, the aliphatic congeners are hardly converted to amines by the Bu_3GeH/PhSH system (unpublished results).

[25] Under radical conditions, tributyltin hydride performs effective reduction of both aromatic and aliphatic azides, but the reductions of the aromatic azides are faster.

[26] It is possible that triazenyl radical adducts from aromatic azides are essentially prone to extrude molecular nitrogen, yielding resonance-stabilized anilinyl radicals, whereas those from aliphatic azides have a fair propensity to give back the added radical and/or act as radical scavengers.

[27] It is worth noting that the use of tris(trimethylsilyl)silane [$(TMS)_3SiH$] instead of our silane/thiol protocol is much less rewarding. A few experiments carried out on azides **1a** and **4a** revealed that the starting azides are not totally consumed even when treated overnight with a 4-fold excess of $(TMS)_3SiH$, which, by the way, is ca. 14 times more expensive than triethylsilane.