Organic LETTERS

Letter

pubs.acs.org/OrgLett

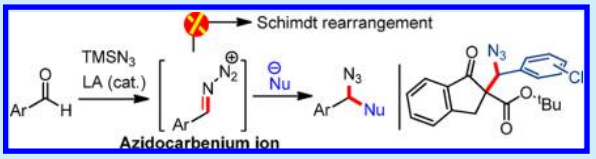
Trapping of Azidocarbenium Ion: A Unique Route for Azide Synthesis

Suman Pramanik and Prasanta Ghorai*

Department of Chemistry, Indian Institute of Science Education and Research Bhopal, Indore By-pass Road, Bhauri, Bhopal 462066, India

Supporting Information

ABSTRACT: For the first time, a sensitive azidocarbenium ion intermediate has been trapped with various nucleophiles to provide azides in excellent chemoselectivity. This provides a novel approach for the chemoselective synthesis of primary and secondary benzyl azides from aldehydes in a one-pot reaction. Enantioselective nucleophilic addition to the azidocarbenium ion has also been initiated.

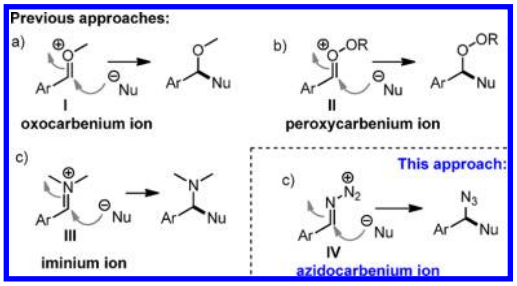


The α-azidocarbenium ion (**IV**, Scheme 1) has been well-known in the literature since the middle half of the twentieth century as an intermediate in Schmidt and related rearrangement reactions.[1] It has already been well established that in such an intermediate the α-azido group stabilizes the carbocation;[2] moreover, ab initio calculations have predicted that the α-azido group can stabilize the α-carbocation better than an α-OH group, albeit to a reduced extent in comparison to the α-NH_2 group.[3] Although there are overwhelming reports for the trapping of the oxocarbenium ion (**I**),[4] the peroxycarbenium ion (**II**),[5] and the iminium ion (**III**)[6] for the synthesis of alkoxides, peroxides, and amines, respectively, the trapping of an analogous azidocarbenium ion (**IV**) for the synthesis of azides has never been developed.[1] The real obstacle to surmount in achieving trapping of the azidocarbenium ion is to stop the Schmidt and related rearrangements driven by the thermodynamically favorable loss of molecular nitrogen (N_2) gas from the azido group (Scheme 2a). Here, we envisioned the unprecedented approach for the trapping of a highly sensitive azidocarbenium ion intermediate (**IV**) with numerous nucleophiles to provide a diverse class of benzylazides from aldehydes with excellent chemoselectivity (Scheme 2b).

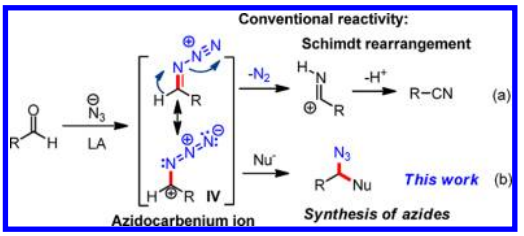
The benzyl azides are valuable intermediates in organic synthesis. These are extensively used in biological studies as a fluorescent probe through its click chemistry.[7] Furthermore, these find application in the synthesis of amines, nitriles and in many other organic transformations.[8] Such azides have been used as important building blocks for the synthesis of other classes of molecules, including natural products containing piperidine[9] and the pyrrolidine core.[10]

In general, the benzyl azides are prepared by nucleophilic substitution of an appropriate benzyl electrophile with azide anions. In this context, recently considerable attention has been paid toward the development of azidation reaction via catalytic S_N1-type (via carbocation intermediate)[11] instead of the traditional stoichiometric S_N2-type[12,13] reaction pathway. However, benzyl alcohols[11a] or alcohol derivatives[11b,c] with electron-deficient substituents such as O_2N-, CN-, CO_2R, etc. are unsuccessful as substrate for such catalytic (S_N1-type) reactions because of the instability of the corresponding carbocationic intermediate (**A**, Scheme 3). For the same reason, our recently developed $FeCl_3$-catalyzed synthesis of homoallylic azides, via an allylation−azidation sequence, also suffer from similar substate scope.[11d] Therefore, we aimed that via an azidocarbenium ion

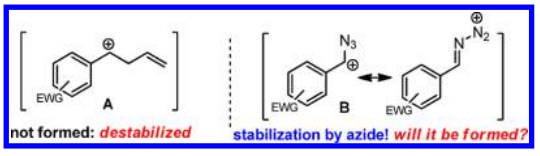
Scheme 1. Chemistry of the α-Stabilized Carbenium Ions



Scheme 2. Chemistry of Azidocarbenium Ion Intermediate



Scheme 3. Benzyl Carbocation vs Azidocarbenium Ion



Received: February 14, 2014
Published: April 4, 2014

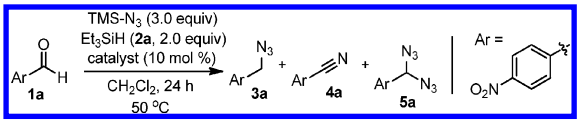
dx.doi.org/10.1021/ol5008235 | Org. Lett. 2014, 16, 2104−2107

(**B**) pathway would eliminate such limitations; the carbocation would get stabilized by the α-azido group which might be sufficient to compensate for the electron-deficiency caused by electron-withdrawing group on the aryl ring.

Recently, a reductive azidation of carbonyls via tosylhydrazones has been developed by Barluenga and co-workers, providing moderate yields of primary and secondary azides.[13] Notably, benzyl azides are not accessible via other methods such as the reactions of carbon nucleophile with electrophilic azides[14] and hydroazidation of alkenes.[15]

We started our investigation of the direct reductive azidation choosing 4-nitro benzaldehyde (**1a**), a challenging substrate for the S_N1-like (via a carbocationic intermediate) reaction conditions, as a model substrate in the presence of TMS-N_3 and Et_3SiH as azide and hydride source, respectively (summarized in Table 1). In the presence of various Lewis acid

Table 1. Optimization of the Reaction Conditions[a]



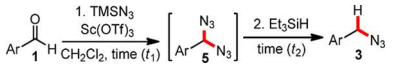
entry	catalysts (10 mol %)	yield of **3a**[b] (%)	**3a**:**4a**[c]
1	$In(OTf)_3$	5	50:50
2	$FeCl_3$	8	9:91
3	$AuCl_3$	0	0:100
4	$Cu(ClO_4)_2$	23	39:61
5	**$Sc(OTf)_3$**	**100 (78)**[d]	**99:1**
6	AgOTf	18	69:31
7	$Bi(OTf)_3$	14	73:27
8	$Cu(OTf)_2$	1	42:58

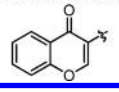
[a]**1** (0.3 mmol), TMS-N_3 (0.9 mmol), catalyst (0.03 mmol) in CH_2Cl_2 at 50 °C for 5 h, then Et_3SiH (0.6 mmol) was added, followed by stirring for 24 h. [b]^1H NMR yield of the reaction mixture using acetophenone as an internal standard. [c]Ratios were determined using ^1H NMR of the reaction mixture. [d]Isolated yields (in parentheses).

catalysts, the addition of $TMSN_3$ and Et_3SiH sequentially provided the mixture of products containing the desired azide (**3a**) along with nitrile (**4a**) and diazide (**5a**)[16] respectively. Interestingly, $Sc(OTf)_3$ as catalyst mainly provided the desired azide (**3a**) along with the diazide (**5a**) which further slowly converted to the azide **3a** on longer duration of the reaction. Since the formation of nitrile (**4a**) completely ceases on addition of excess TMS-N_3, we preferred to convert the aldehyde to diazide **5a** by adding excess $TMSN_3$ (by TLC) followed by conversion of diazide **5a** to azide **3a** by the addition of Et_3SiH. Thus, the chemoselectivity of azidation over nitrile formation was controlled. Although the reaction proceeds well in a number of solvents, CH_2Cl_2 was identified as optimal for both the steps to proceed with high chemoselectivity.

With these optimized reaction conditions identified, we examined the reductive azidation of a wide variety of aldehydes as summarized in Table 2. Both electron-deficient and electron-rich aldehydes are effective for the current reaction. Aromatic aldehydes with other electron-deficient substituents such as *m*-O_2N, *p*-CN, *p*-EtO_2C, *m*-F_3C, 3,5-di-F_3C, fluoro, chloro, bromo, and phenyl react at rt to 50 °C to provide the desired benzyl azides (**3b**–**j**, entries 2–10) in good yields with excellent chemoselectivity. Further, aromatic aldehydes with electron-rich substituents such as methyl, methoxy, and benzyloxy react even more smoothly to provide the desired products (**3k**–**m**,

Table 2. Scope of Aldehydes for Reductive Azidation[a]



entry	cond[a]	Ar-, **1**	t_1/t_2 (h)	**3**, (%)[b]
1[e]	A	*p*-O_2N-C_6H_4- (**1a**)	5/24	**3a**, 78
2[e]	B	*m*-O_2N-C_6H_4- (**1b**)	4/14	**3b**, 91
3	A	*p*-NC-C_6H_4- (**1c**)	3/32	**3c**, 97
4[e]	B	*p*-EtO_2C-C_6H_4- (**1d**)	0.5/15	**3d**, 57
5	B	*m*-F_3C-C_6H_4- (**1e**)	1/12	**3e**, 87
6	B	3,5-$(F_3C)_2$-C_6H_3- (**1f**)	6/24	**3f**, 90
7	C	*p*-F-C_6H_4- (**1g**)	1/0.5	**3g**, 80
8	C	*p*-Cl-C_6H_4- (**1h**)	0.5/1	**3h**, 92
9	C	*o*-Br-C_6H_4- (**1i**)	0.5/1.5	**3i**, 94
10	C	*p*-Ph-C_6H_4- (**1j**)	1/1	**3j**, 95
11	C	*p*-Me-C_6H_4- (**1k**)	0.5/1	**3k**, 83
12	C	*p*-MeO-C_6H_4- (**1l**)	1.5[c]/1	**3l**, 85
13	C	*m*-BnO-C_6H_4- (**1m**)	1/0.5	**3m**, 95
14	C	C_6H_5- (**1n**)	0.5/1	**3n**, 86
15	C	α-Naphthyl- (**1o**)	0.5/15	**3o**, 80
16	C	2- Fluorene- (**1p**)	1/8	**3p**, 90
17[d]	C	2-Thyal- (**1q**)	0.3/0.3	**3q**, 88
18[d]	C	3-*N*-Boc-indole (**1r**)	0.6/8	**3r**, 70
19[d]	B	 (**1s**)	1/1	**3s**, 55

[a]**1** (1.0 mmol), TMS-N_3 (2.8 mmol), $Sc(OTf)_3$ (5 mol %) in CH_2Cl_2, at 50 °C (A) or rt (B) or 0 °C (C) for t_1 h, then nucleophile **2a** was added at 50 °C for conditions A and B or at rt for condition C and stirred for t_2 h. [b]Isolated yield. [c]Step 1 was carried out at −10 °C instead of 0 °C. [d]AgOTf (10 mol %) was used. [e]10 mol % $Sc(OTf)_3$ was used.

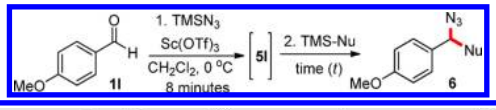
respectively, entries 11–13) in good yields. Benzyl as well as naphthaldehydes are also equally effective for the current process (entries 14–16). The reductive azidation of heteroaromatic aldehydes like thiophene-2-carboxaldehyde, *N*-Boc-indole-3-carboxaldehyde and chroman-2-en-4-one-3-carbaldehyde also proceeded smoothly using AgOTf instead of $Sc(OTf)_3$ as catalyst to furnish the corresponding azides (entries 17–19). Unfortunately, aliphatic aldehydes are not a suitable substrate for reductive azidation.

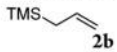
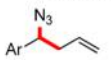
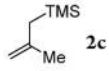
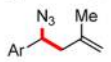
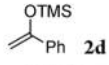
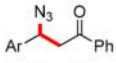
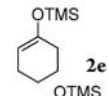
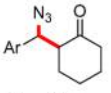
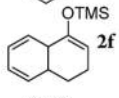
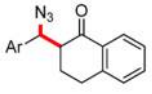
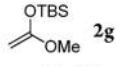
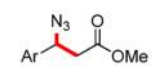
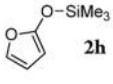
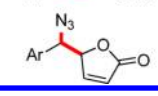
After successful reductive azidation, we turned our attention toward C–C bond formation with azidocarbenium ion for the synthesis of secondary benzyl azides (Table 3). As shown, azidocarbenium ion derived from *p*-MeO benzaldehyde was trapped with various silanes (**2b**,**c**), silyl enol ethers (**2d**–**f**), and silyl ketene acetal (**2g**) to provide a variety of secondary azides such as homoallylic azides (**6a**,**b**), β-azido carbonyls (**6c**–**e**), and β-azido esters (**6f**) in good yields and with excellent chemoselectivities (entries 1–6, respectively). We extended the present methodology to silyloxy furan (**2h**) as nucleophile to provide vinylogous addition product **6g** (entry 7). Notably, most of these synthesized compounds are unprecedented in the literature.

Further potential utility of such electrophilic α-azidobenzyl cations generated from diazides was extended to the functionalization of nucleophilic β-keto esters (as shown in Scheme 4). For example, β-keto esters of cyclopentanone- (**7a**,**b**), indanone- (**7c**), and cyclohexanone- (**7d**) were evaluated and furnished the corresponding products **8a**–**f**, having an *all carbon quaternary*

dx.doi.org/10.1021/ol5008235 | Org. Lett. 2014, 16, 2104–2107

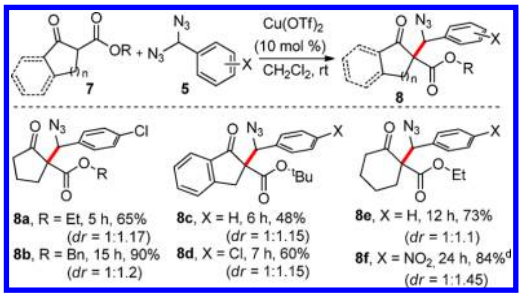
Table 3. Scope of Nucleophiles for the Synthesis of Azides[a]



entry	nucleophile	t (h)	product	(%)[b]
1	 2b	2.5	 6a	75 (88)[c]
2	 2c	3	 6b	68 (90)[c]
3	 2d	1.5	 6c	66
4	 2e	1.5	 6d	76
5	 2f	3	 6e	65
6	 2g	1	 6f	70
7	 2h	1	 6g	71

[a]**1l** (1.0 mmol), $TMSN_3$ (2.8 mmol), and $Sc(OTf)_3$ (10 mol %) were stirred at 0 °C in CH_2Cl_2 for 8 min, nucleophile (2.0 mmol) was added, the temperature was increased to rt, and the mixture was stirred for time *t*. [b]Isolated yield. [c]The yield in parentheses refers to the reaction when carried out from *gem*-diazide **5l** instead of **1l** (see the Supporting Information).

Scheme 4. Synthesis of β-Azidodicarbonyls[a–c]



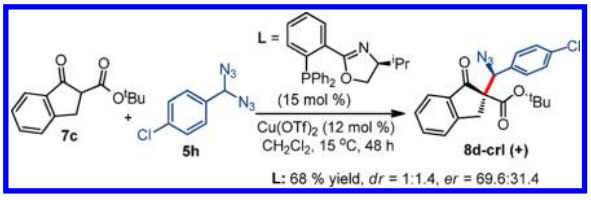
[a]**7** (0.5 mmol), *gem*-diazide (**5**, 0.75 mmol), $Cu(OTf)_2$ (10 mol %) in CH_2Cl_2, 0 °C for 15 min, then at rt. [b]Isolated yield. [c]dr was determined from the ^1H NMR of the reaction mixture. [d]Reaction was carried out at 50 °C.

carbon center α to the azidobenzyl group, in good yields and with excellent chemoselectivity. To our surprise, isolated diazides (**5**) instead of in situ formed diazides (as was the case in Table 3) provided better yields; moreover, $Cu(OTf)_2$ showed superior reactivity instead of $Sc(OTf)_3$ as catalyst in this particular case.

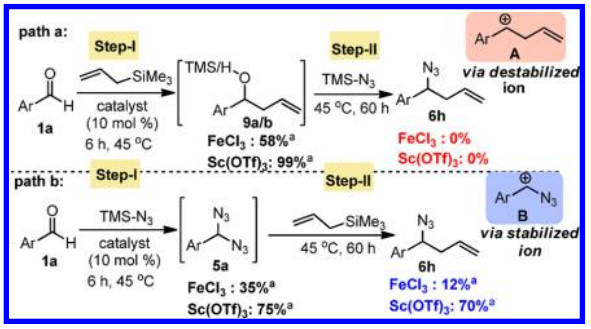
Next, we became interested in examining the enantioselective variant of the above developed reactions. As shown in Scheme 5, a preliminary attempt to provide the proof of concept has been investigated using catalytic $Cu(OTf)_2$ in the presence of catalytic ^{i}Pr-PHOX (**L**), as chiral ligand, providing an enantioselective $C(sp^3)$–$CH(N_3)Ar$ product (**8d-crl**) in good yield (68%) and with acceptable enantioselectivity (~40% ee).

The advantage of the current azidation–allylation sequence over our previous report of an allylation–azidation sequence of aldehydes (**1a**)[11d] has also been demonstrated (summarized in Scheme 6). As shown, in the presence of $FeCl_3$, as well as

Scheme 5. Preliminary Result of Enantioselective Variant



Scheme 6. Benzyl Carbocation vs Azidocarbenium Ion[a]

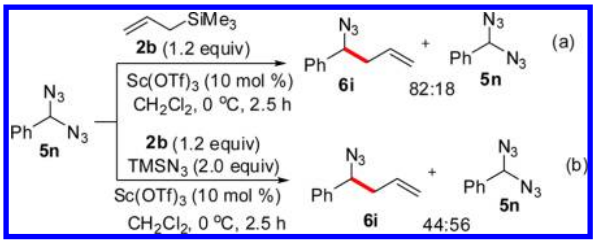


[a]Yields are based on ^1H NMR studies of reaction mixture.

$Sc(OTf)_3$ catalyst, following the previous protocol (path a), the in situ formed homoallyl alcohol/silyl ether intermediates (**9a/b**) did not convert to the corresponding azide **6h**. These results reflect the difficulty in the formation of the corresponding carbocation **A**. On the other hand, the current azidation followed by allylation using the same catalysts (path b) provided the desired azide **6h**. The easy formation of azidocarbenium ion intermediate **B** most likely enabled this process.

Furthermore, a common azide ion inhibition experiment was carried out to observe the effect of $TMS\text{-}N_3$ in the above reaction (Scheme 7). We observed that the substitution of diazide (**5n**)

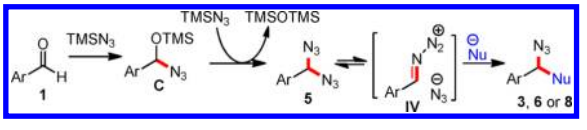
Scheme 7. Common Azide Ion Inhibition Experiment



with allyl-TMS is much slower in the presence of excess amount of $TMS\text{-}N_3$. An excess of $TMS\text{-}N_3$ likely surrounds the in situ formed azidocarbenium ion (through a "contact ion pair"[2c]) which prevents the nucleophilic attack by the allylic anion. This is also an indirect indication for a stepwise reaction mechanism through the generation of an α-azidocarbenium ion followed by nucleophilic addition reaction.

The plausible mechanism for the current reaction is proposed in Scheme 8. Azidation of the aldehyde using $TMS\text{-}N_3$ forms an α-azidosilyl ether (**C**) which undergoes further azidation to give

Scheme 8. Proposed Reaction Mechanism



dx.doi.org/10.1021/ol5008235 | Org. Lett. 2014, 16, 2104–2107

gem-diazide (**5**). The interesting feature of this strategy is that one of the azide functionalities is being activated by another azide group in the presence of a Lewis acid to form the α-azidocarbenium ion species (**IV**), which is then trapped by organosilane to afford the azide **3**, **6**, or **8**.

In summary, we have developed an unprecedented approach for the trapping of sensitive α-azidocarbenium ions with various nucleophiles. This provided a convenient, one-pot, catalytic method for the chemoselective synthesis of primary and secondary benzyl azides directly from aldehydes. The aldehydes are first converted to diazide which in situ dissociates to provide the α-azidocarbenium ion that is being trapped by various nucleophiles. Interestingly, the favorable Schmidt rearrangement of such intermediates has been overcome. Further investigations toward the scope and limitations of this methodology for the synthesis of various azides are in progress.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, characterization data, and copies of NMR spectra for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: pghorai@iiserb.ac.in.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work has been supported by BRNS, DAE, India, through a DAE Young Scientist Research Award Grant. We are grateful to IISER Bhopal for additional support. We are thankful to Dr. Deepak Chopra for his assistance. S.P. thanks CSIR, New Delhi, India, for a fellowship.

■ REFERENCES

(1) (a) Schmidt, K. F. *Z. Angew. Chem.* **1923**, *36*, 511−524. (b) Schmidt, K. F. *Chem. Ber.* **1924**, *57*, 704−706. (c) Smith, P. A. S.; Horwitz, J. P. *J. Am. Chem. Soc.* **1950**, *72*, 3718−3722. For recent examples, see: (d) Rokade, B. V.; Prabhu, K. R. *J. Org. Chem.* **2012**, *77*, 5364−5370.

(2) Stabilization of the carbocation by an α-azido group: (a) Bach, R. D.; Wolber, G. J. *J. Org. Chem.* **1982**, *47*, 239−245. (b) Amyes, T. L.; Richard, J. P. *J. Am. Chem. Soc.* **1991**, *113*, 1867−1869. (c) Richard, J. P.; Amyes, T. L.; Jagannadham, V.; Lee, Y.-G.; Rice, D. J. *J. Am. Chem. Soc.* **1995**, *117*, 5198−5205. (d) Richard, J. P.; Amyes, T. L.; Toteva, M. M. *Acc. Chem. Res.* **2001**, *34*, 981−988.

(3) Hoz, S.; Wolk, J. L. *Tetrahedron Lett.* **1990**, *31*, 4085−4088.

(4) Oxocarbenium ion: (a) Woods, R. J.; Andrews, C. W.; Bowen, J. P. *J. Am. Chem. Soc.* **1992**, *114*, 859−864. (b) Larsen, C. H.; Ridgway, B. H.; Shaw, J. T.; Woerpel, K. A. *J. Am. Chem. Soc.* **1999**, *121*, 12208−12209. (c) Albury, A. M. M.; Jennings, M. P. *J. Org. Chem.* **2012**, *77*, 6929−6936. (d) Tran, V. T.; Woerpel, K. A. *J. Org. Chem.* **2013**, *78*, 6609−6621.

(5) Peroxycarbenium ion: (a) Dussault, P. H.; Lee, I. Q. *J. Am. Chem. Soc.* **1993**, *115*, 6458−6459. (b) Dussault, P. H.; Liu, X. *Org. Lett.* **1999**, *1*, 1391−1393. (c) Dussault, P. H.; Lee, I. Q.; Lee, H.-J.; Lee, R. J.; Niu, Q. J.; Schultz, J. A.; Zope, U. R. *J. Org. Chem.* **2000**, *65*, 8407−8414. (d) Ramirez, A.; Woerpel, K. A. *Org. Lett.* **2005**, *7*, 4617−4620. (e) Dai, P.; Trullinger, T. K.; Liu, X.; Dussault, P. H. *J. Org. Chem.* **2006**, *71*, 2283−2292.

(6) Iminium ion: (a) Erkkilä, A.; Majander, I.; Pihko, P. M. *Chem. Rev.* **2007**, *107*, 5416−5470. (b) Dell'Amico, L.; Albrecht, Ł.; Naicker, T.; Poulsen, P. H.; Jørgensen, K. A. *J. Am. Chem. Soc.* **2013**, *135*, 8063−8070. (c) Huang, J.; Zhao, L.; Liu, Y.; Cao, W.; Wu, X. *Org. Lett.* **2013**, *15*, 4338−4341. (d) Paradisi, E.; Righi, P.; Mazzanti, A.; Ranieri, S.; Bencivenni, G. *Chem. Commun.* **2012**, *48*, 11178−11180.

(7) (a) Wang, Q.; Chan, T. R.; Hilgraf, R.; Fokin, V. V.; Sharpless, K. B. *J. Am. Chem. Soc.* **2003**, *125*, 3192−3193. (b) Zhou, Z.; Fahrni, C. J. *J. Am. Chem. Soc.* **2004**, *126*, 8862−8863. (c) Friscourt, F.; Fahrni, C. J.; Boons, G.-J. *J. Am. Chem. Soc.* **2012**, *134*, 18809−18815.

(8) For an excellent review of the diverse chemistry of organoazides, see: (a) Myers, E. L.; Raines, R. T. *Angew. Chem., Int. Ed.* **2009**, *48*, 2359−2363. (b) Bräse, S.; Gil, C.; Knepper, K.; Zimmermann, V. *Angew. Chem., Int. Ed.* **2005**, *44*, 5188−5240. For recent articles, see: (c) Kulkarni, S. S.; Hu, X.; Manetsch, R. *Chem. Commun.* **2013**, *49*, 1193−1195. (d) Wang, Y.-F.; Chiba, S. *J. Am. Chem. Soc.* **2009**, *131*, 12570−12572. (e) Hui, B. W.-Q.; Chiba, S. *Org. Lett.* **2009**, *11*, 729−732. (f) Mahoney, J. M.; Smith, C. R.; Johnston, J. N. *J. Am. Chem. Soc.* **2005**, *127*, 1354−1355.

(9) (a) Girard, S.; Robins, R. J.; Villiéras, J.; Lebreton, J. *Tetrahedron Lett.* **2000**, *41*, 9245−9249. (b) Spangenberg, T.; Breit, B.; Mann, A. *Org. Lett.* **2009**, *11*, 261−264. (c) Coia, N.; Mokhtari, N.; Vasse, J.-L.; Szymoniak, J. *Org. Lett.* **2011**, *13*, 6292−6295.

(10) (a) Jego, J. M.; Carboni, B.; Vaultier, M.; Carrié, R. *Chem. Commun.* **1989**, 142−143. (b) Jego, J. M.; Carboni, B.; Vaultier, M. *Bull. Soc. Chim. Fr.* **1992**, *129*, 554−565.

(11) For azidation of benzyl alcohol (via S_N1 pathway), see: (a) Sampath Kumar, H. M.; Subba Reddy, B. V.; Anjaneyulu, S.; Yadav, J. S. *Tetrahedron Lett.* **1998**, *39*, 7385−7388. (b) Chan, L. Y.; Kim, S.; Chung, W. T.; Long, C.; Kim, S. *Synlett* **2011**, 415−419. (c) Sawama, Y.; Nagata, S.; Yabe, Y.; Morita, K.; Monguchi, Y.; Sajiki, H. *Chem.—Eur. J.* **2012**, *18*, 16608−16611. (d) Pramanik, S.; Ghorai, P. *RSC Adv.* **2013**, *3*, 23157−23165.

(12) For azidation of alcohols (via S_N2 pathway), see: (a) Thompson, A. S.; Humphrey, G. R.; DeMarco, A. M.; Mathre, D. J.; Grabowski, E. J. J. *J. Org. Chem.* **1993**, *58*, 5886−5888. (b) Mizuno, M.; Shioiri, T. *Chem. Commun.* **1997**, 2165−2166. (c) Iranpoor, N.; Firouzabadi, H.; Akhlaghinia, B.; Nowrouzi, N. *Tetrahedron Lett.* **2004**, *45*, 3291−3294. (d) Rad, M. N. S.; Behrouzb, S.; Khalafi-Nezhad, A. *Tetrahedron Lett.* **2007**, *48*, 3445−3449. (e) Kuroda, K.; Hayashia, Y.; Mukaiyama, T. *Tetrahedron* **2007**, *63*, 6358−6364.

(13) For reductive azidation, see: Barluenga, J.; Tomás-Gamasa, M.; Valdés, C. *Angew. Chem., Int. Ed.* **2012**, *51*, 5950−5952.

(14) (a) Evans, D. A.; Britton, T. C. *J. Am. Chem. Soc.* **1987**, *109*, 6881−6883. (b) Benati, L.; Calestani, G.; Nanni, D.; Spagnolo, P. *J. Org. Chem.* **1998**, *63*, 4679−4684. (c) Vita, M. V.; Waser, J. *Org. Lett.* **2013**, *15*, 3246−3249.

(15) (a) Waser, J.; Nambu, H.; Carreira, E. M. *J. Am. Chem. Soc.* **2005**, *127*, 8294−8295. (b) Waser, J.; Gaspar, B.; Nambu, H.; Carreira, E. M. *J. Am. Chem. Soc.* **2006**, *128*, 11693−11712. (c) Kapat, A.; Köning, A.; Montermini, F.; Renaud, P. *J. Am. Chem. Soc.* **2011**, *133*, 13890−13893.

(16) For early examples of diazide chemistry, see: (a) Sommers, A. H.; Barnes, J. D. *J. Am. Chem. Soc.* **1957**, *79*, 3491−3492. (b) Barash, L.; Wasserman, E.; Yager, W. A. *J. Am. Chem. Soc.* **1967**, *89*, 3931−3932. (c) Moriarty, R. M.; Serridge, P. *J. Am. Chem. Soc.* **1971**, *93*, 1534−1535. (d) Nishiyama, K.; Watanabe, A. *Chem. Lett.* **1984**, 455−458.