CHEMISTRY
A European Journal

A Journal of
ChemPubSoc Europe

Accepted Article

Title: Silver-Catalyzed [2+1] Cyclopropenation of Alkynes with Unstable Diazoalkanes: N-Nosylhydrazones as Room-Temperature Decomposiable Diazo Surrogates

Authors: Xihe Bi, Zhaohong Liu, Qiangqiang Li, and Peiqiu Liao

To be cited as: *Chem. Eur. J.* 10.1002/chem.201605335

Link to VoR: http://dx.doi.org/10.1002/chem.201605335

Supported by
ACES

WILEY-VCH

CHEMISTRY A EUROPEAN JOURNAL

COMMUNICATION

DOI: 10.1002/chem.200((will be filled in by the editorial staff))

Silver-Catalyzed [2+1] Cyclopropenation of Alkynes with Unstable Diazoalkanes: *N*-Nosylhydrazones as Room-Temperature Decomposable Diazo Surrogates

Zhaohong Liu,[a] Qiangqiang Li,[a] Peiqiu Liao[a] and Xihe Bi*[a][b]

Abstract: The [2+1] cycloaddition of alkynes with diazo compounds represents one of the most powerful and reliable methods for the construction of cyclopropenes. However, it remains a formidable challenge to accomplish the cyclopropenation of alkynes with non-stabilized diazoalkanes, owing to the fact that such compounds are unstable and prone to detonation. Here, we report a general silver-catalyzed general cyclopropenation reaction of alkynes with unstable diazoalkanes, by for the first time discovery and application of *N*-nosylhydrazones as room-temperature decomposiable diazo surrogates. This method allows for efficiently assembling a wide variety of cyclopropene derivatives that are otherwise difficult to access by conventional methods.

Amongst small ring molecules, cyclopropenes are arguably the most strained single ring organic molecules, and occupy a unique position in hydrocarbon chemistry.[1] The high intrinsic energy of cyclopropene molecules renders them to be versatile synthetic imtermediates, but in turn limits their synthesis to a few practically useful cyclopropenation methodologies.[2] Among these, the [2+1]-cycloaddition of alkynes with diazo compounds is a classical, yet reliable, powerful and therefore widely used route.[2][3] However, the diazo compounds directly used in such reactions were all limited to those stabilized with electron-withdrawing[4] or trimethylsilyl groups.[5] The general [2+1]-cycloaddition of alkynes with unstable diazoalkanes remains elusive, because of their inherent characteristics such as being prone to explode leading to the difficulty in preparation and handling.[6] To overcome this drawback, various diazo surrogates have been synthetically explored and significantly expanded the repertoire of diazo-participating reactions.[7] However, the diazo surrogates applied in [2+1] cyclopropenation of alkynes ar highly limited,[8]-[11] because the dissociation conditions of mos diazo surrogates are hardly compatible with the followin cyclopropenation process. As a result, only a few methods ar known in the literature, including Warkentin's photolysis of 2 alkoxy-3,4-oxadiazolines,[8] Gevorgyan's rhodium-catalyzed ring opening of pyridotriazoles,[9] Carreira's in situ conversion c trifluoroethylamine into trifluoromethyldiazomethane in aqueou media,[10] and Valdés' base-promoted decomposition of 2,2,2 trifluoroacetophenone tosylhydrazones[11] (Figure 1). Limitatio to electron-withdrawing CF_3 group or specific diazo precursor remains as major disadvantages in these methods. To establish general [2+1] cyclopropenation reaction of alkynes with unstabl diazoalkanes, two issues must be overcome simultaneously, (i discovery of a diazo surrogate capable of dissociating under mil conditions, (ii) finding a catalyst able to activate both diaz species and alkynes. Silver catalysis has recently attracted muc attention in organic synthesis, especially its unique catalyti performance often observed in many reactions.[12] While th silver-catalyzed carbene transfer reactions have been les developed to date, the pioneering reports by Davies and co-work described silver-catalyzed cyclopropanation of alkenes[13] an cyclopropenation of internal alkynes[14] with electron-withdrawin group (EWG)-stabilized diazo compounds. As our continue studies on silver-catalyzed reactions of alkynes,[15] we here repo our studies of silver-catalyzed cyclopropenation of alkynes b discovering *N*-nosylhydrazones as room-temperatur decomposiable diazo surrogates.

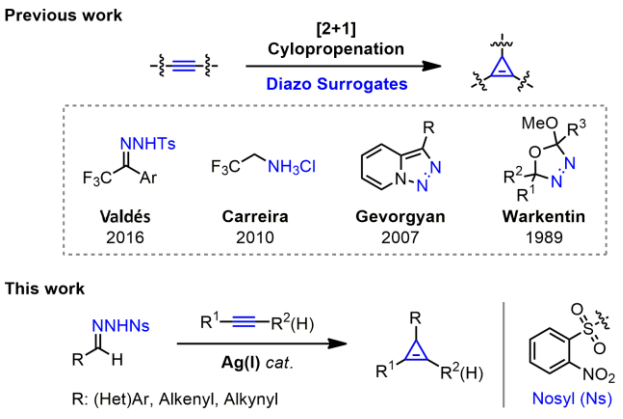


Figure 1. [2+1] Cylopropenation of alkynes with diazo surrogates.

N-tosylhydrazones represent the most synthetically exploited diazo surrogates in the past decade, as demonstrated by the rapidly expanding repertoire of their transformations.[16] However,

[*] Z. Liu, Q. Li, Dr. P. Liao, Prof. X. Bi
Jilin Province Key Laboratory of Organic Functional Molecular Design & Synthesis
Department of Chemistry
Northeast Normal University
Changchun 130024, China
E-mail: bixh507@nenu.edu.cn
Homepage: http://www.bigroup.com.cn/

Prof. X. Bi
State Key Laboratory of Elemento-Organic Chemistry
Nankai University, Tianjin 300071, China

[**] Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201xxxxxx.((Please delete if not appropriate))

10.1002/chem.201605335

the high temperature (> 70 ℃) required for their dissociation into diazo species severely hinders the synthetic extension of *N*-tosylhydrazones, especially to the synthetic areas disfavoring high temperature. This hindrance is evident from the different outcomes observed in the reactions of diazo compounds with boronic acids as reported by Ley[17a] and Barluenga,[17b] where the former achieved boron insertion products based on flow-generated diazo compounds at 25 ℃, whereas the later obtained deboronated products because of the high dissociation temperature of *N*-tosylhydrazones. *N*-nosylhydrazones, as one class of *N*-sulfonylhydrazones, have been considering simply as a faster decomposable alternative to *N*-tosylhydrazones, rather than low-temperature diazo surrogates.[18] We[19] and others[20] have previously reported the rapid decomposition of *o*-nosylhydrazides at room temperature. Based on this observation, we initiated the study on the dissociation of *N*-nosylhydrazone **1a** and *N*-tosylhydrazone **1a'**, respectively, at 25 ℃ in the presence of NaH. As shown in Figure 2a, the former smoothly released 4-chlorophenyl diazomethane as a function of time, whereas the latter remained intact within 24 h. *To the best of our knowledge, this is the first report unraveling N-nosylhydrazones dissociable at room temperature.* Besides, slightly increasing the temperature of cycloprpenation step to 40 ℃ remarkably raised the yield of product **3a** to 85%. Furthermore, the silver salt such as AgOTf was identified as the most effective catalyst for the cyclopropenation of alkynes with *N*-nosylhydrazones. In contrast, other tested carbene transfer catalysts either gave low yields (*e.g.*, $Rh_2(Oct)_4$, 42%) or were totally non-effective (*e.g.*, $Zn(OTf)_2$, $Cu(OTf)_2$, $Pd(OAc)_2$) (Figure 2b) (For details, see supporting information).

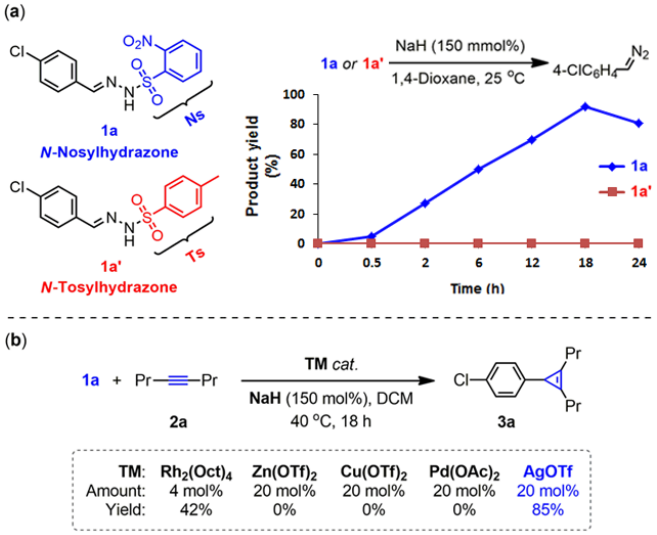
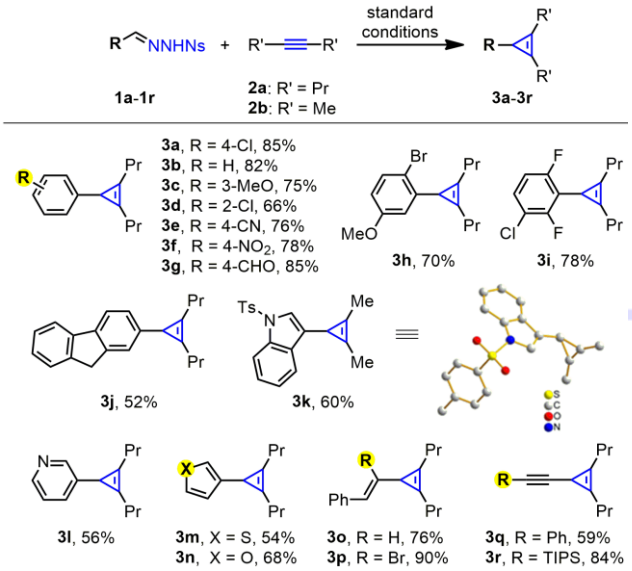


Figure 2. (**a**) Base-promoted dissociation of *N*-nosylhydrazone **1a** and *N*-tosylhydrazone **1a'** at 25 ℃. (**b**) Optimization of the reaction conditions.

With the optimal conditions in hand, we next explored the substrate scope with regard to *N*-nosylhydrazones. As depicted in Scheme 1, a range of structurally varied *N*-nosylhydrazones were applicable in this silver-catalyzed [2+1] cylopropenation of alkynes. Both aromatic and aliphatic (alkenyl, alkynyl) *N*-nosylhydrazones were readily accommodated in this protocol. For example, a variety of substituted aryl *N*-nosylhydrazones (**1a**–**1i**) were able to react with 4-octyne, affording the corresponding cyclopropene products (**3a**–**3i**) in good-to-excellent yields (66%–85%), irrespective of the electronic effect and/or the position of the substituents on the phenyl ring. The functional group tolerance was noteworthy, as the formyl, nitro, cyano, and halo groups were all well tolerated. In addition, this protocol could be applied to the fused aryl such as fluorine-substituted substrate **1j**, albeit with a slightly decreased yield (**3j**, 52%). *N*-nosylhydradrazones having a heteroaryl group such as indole, pyridine, thiophene, and furan also proved to be effective partners (**3k**–**3n**, 54%–68%). The structure of cyclopropenes was unambiguously confirmed by the single-crystal X-ray analysis of product **3k**. Furthermore, *N*-nosylhydrazones derived from α,*β*-unsaturated aldehydes containing a double bond or a triple bond were effectively used, providing the corresponding cyclopropenes (**3o**–**3r**) in good-to-excellent yields (59%–90%). It is wort mentioning that the alkynyl *N*-tosylhydradrazones treated by bas were prone to form pyrazoles by intramolecular cyclization,[2 while this problem was conquered using *N*-nosylhydradrazones In addition, some experiments have been carried out and reveale *N*-nosylhydradrazones derived from enolizable aldehydes c ketones were not suitable for this transformation. For example, N nosylhydrazides derived from 3-phenylpropanal or acetophenon decomposed to give a mixture of corresponding alkene and azin products, but no cyclopropene products could be detected.

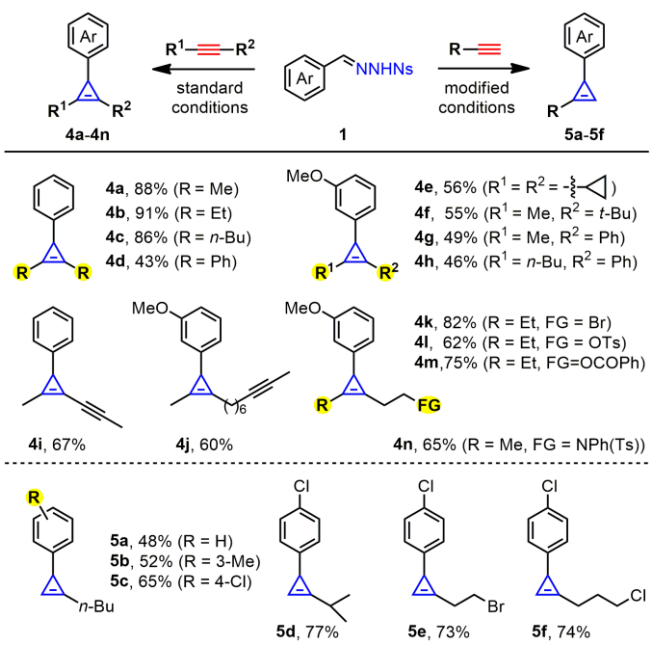


Scheme 1. Substrate scope of *N*-nosylhydrazones. Standard conditions: *N*-nosylhydrazone (0.3 mmol), NaH (0.45 mmol) and CH_2Cl_2 (3.0 mL) were stirred at rt for 1 h, then alkyne (0.6 mmol) and AgOTf (0.06 mmol) were added, and stirred at 40 °C for 18 h. **3n**: *t*-BuOLi was used as base..

We next sought to investigate the scope of alkynes in thi silver-catalyzed cycloaddition reaction (Scheme 2). The substrat scope was broad and all the tested internal alkynes underwent the cyclopropenation with *N*-nosylhydrazones to afford the corresponding cyclopropenes (**4a**–**4n**) with useful efficiencies (43%–91% yields). A remarkable steric hindrance effect of alkyne substrates on the cyclopropenation reaction was observed. For example, the linear alkynes generally gave high yields (**4a**–**4c**, 86%–91%), whereas those with branched chains or a bulky phenyl ring led to gradually decreased product yields (**4d**–**4h**, 43%–56%). Notably, the most bulky 1,2-diphenylethyne also proved to be reactive, albeit with AgOTFA as catalyst. Diverse functionalities, including alkynyl, halogen, ester, and amino

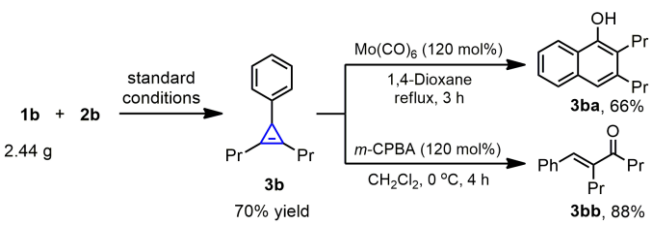
10.1002/chem.201605335

groups, were well tolerant, thus affording a range of functionalized cyclopropenes (**4i**–**4n**, 60%–82%). The tolerance of bromo group in the presence of a halophilic silver catalyst was especially noteworthy.[22] Furthermore, under slightly modified conditions (Ag_2CO_3 as catalyst, highly diluted reaction solution), terminal alkynes also proved to be suitable reaction partners in this silver-catalyzed protocol, which afforded a group of difficult to be synthesized 1-alkyl-3-aryl cyclopropenes in good yields (**5a**–**5f**, 48%–77%). Notably, Wang and coworkers reported the reaction of terminal alkynes with *N*-tosylhydrazones by copper catalysis afforded allenes,[23] clearly demonstrating the different catalytic activity of silver catalyst.

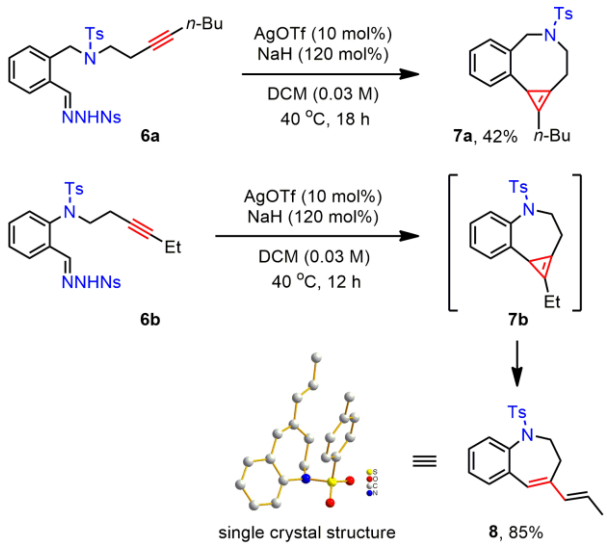


Scheme 2. Substrate scope of alkynes. Modified conditions: *N*-nosylhydrazone (0.5 mmol), NaH (0.75 mmol) and CH_2Cl_2 (10.0 mL) were stirred at rt for 1 h, then terminal alkynes (5.0 mmol) and Ag_2CO_3 (0.15 mmol) were added, and stirred at 40 ℃ for 18 h. **4d**: AgOTFA (20 mol%) was used.

To demonstrate the scalability of this protocol, we conducted a reaction on large scale, and observed that the gram-scale synthesis with 2.44 g of *N*-nosylhydrazone **1b** proceeded well under the standard conditions. Further, the synthetic utility of cyclopropenes was demonstrated by the rearrangement of **3b** into naphthol **3ba**[24] and the peracid oxidation leading to α-alkylchalcone **3bb**,[25] respectively.

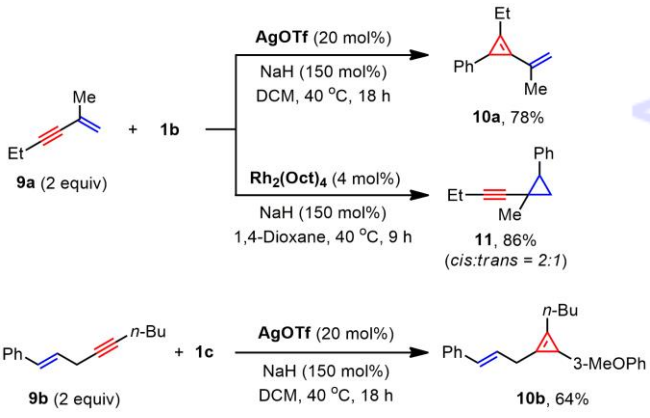


The high strain energy of ring-fused cyclopropenes makes their synthesis and isolation to be a difficult task.[26] We attempted to apply our method to attain this aim. After several trials, we eventually isolated an eight-member-fused cyclopropene **7a** in a moderate yield (42%) starting from *N*-nosylhydrazone **6a**, in a diluted solution (0.03 M) (Figure 2). By contrast, the reaction of substrate **6b**, which has one carbon atom less in the alkyl chain, did not cease in the step of forming fused cyclopropene **7b**, while gave a pharmacologically relevant benzo[*b*]azepine **8** in 85% yield by a regioselective ring opening reaction.[27] The structure of **8** was confirmed by X-ray crystallographic analysis.



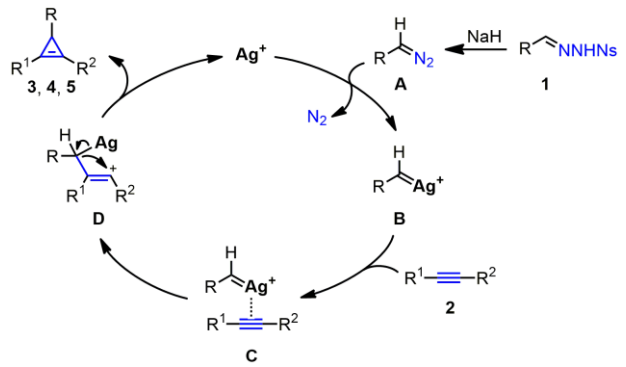
Scheme 3. Intramolecular reaction..

The chemoselectivity of enyne systems, *i.e.*, cyclopropanatio *vs* cyclopropenation, was studied (Scheme 4). We observed tha the reaction of enyne **9a** with *N*-nosylhydrazone **1b** by silve catalysis chemospecifically produced cyclopropene **10a** as a sol product. Interestingly, the same reaction could be switched t cyclopropanation simply by replacing the silver catalyst with rhodium catalyst, which afforded alkynyl cyclopropane **11** with *cis*:*trans* ratio of *2*:*1*. The non-conjugated enyne **9b** displayed th same chemoselectivity as the conjugated enyne to affor cyclopropene **10b**. Notably, the silver-based catalysis does nc always favor the cyclopropenation selectivity of enynes, as th Davies group previously observed a complete cyclopropanation i a silver-catalyzed reaction of enyne **9a** with α-diazocarbony compounds.[14] A comparison of our results with those of Davies clearly demonstrated the different reactivity of non-stabilize diazoalkanes and α-diazocarbonyl compounds.



Scheme 4. Chemoselectivity of enynes.

Based on the experimental results and related precedents,[28] we suggest a presumed mechanistic description for the silver-catalyzed cyclopropenation reaction of alkynes with non-stabilized diazoalkanes (Scheme 5). Base-promoted dissociation of *N*-nosylhydrazones **1** first occurs to generate unstable diazo compound **A**, which readily undergoes dinitrogen extrusion by a silver catalyst to give a transient silver carbenoid **B**.[28a] Subsequently, coordination to the carbon-carbon triple bond of alkynes takes place affording the coordinated complex **C**. Following the migratory insertion, an organosilver intermediate **D** is generated. Finally, the cyclopropene products are produced, with the regeneration of Ag(I) catalyst for the next catalytic cycle. Apparently, the function of the silver salts as a robust catalyst probably could be ascribed to the superior alkynophilicity of in situ formed silver carbenoid.[12]



Scheme 5. Mechanistic proposal.

In summary, we have developed the first silver-catalyzed general [2+1] cyclopropenation reaction of alkynes with unstable diazoalkanes, by for the first time discovering the capability of *N*-nosylhydrazones acting as room-temperature diazo surrogates. The newly developed method features in broad substrate scope, high reaction efficiency, good functional group tolerance, and unexpected cyclopropenation selectivity in enyne systems, thus demonstrating its remarkable synthetic potency. Furthermore, a variety of cyclopropene derivatives that are otherwise difficult to access by conventional methods were obtained in generally good yields. Further expansion of this *N*-nosylhydrazone strategy combined with silver catalysis to asymmetric synthesis and other synthetic areas is currently under way and will be reported in due course.

Acknowledgements

This work was supported by the NSFC (21522202, 21502017, 21372038), the Ministry of Education of the People's Republic of China (NCET-13-0714), the Jilin Provincial Research Foundation for the Basic Research (20140519008JH), Fundamental Research Funds for Central Universities (2412015BJ005, 2412015KJ013, 2412016KJ040), and the Jilin Province Key Laboratory of Organic Functional Molecular Design & Synthesis (No. 130028658).

Keywords: *N*-nosylhydrazones • alkynes • cyclopropenation • silver-catalyzed • diazo surrogates

[1] For selected reviews on cyclopropenes, see: a) F. L. Carter, V. L. Frampton, *Chem. Rev.* **1964**, *64*, 497; b) M. S. Baird, *Chem. Rev.* **2003**, *103*, 1271; c) R. Walsh, *Chem. Soc. Rev.* **2005**, *34*, 714; d) M. Rubin, M. Rubina, V. Gevorgyan, *Synthesis* **2006**, 1221; e) M. Rubin, M. Rubina, V. Gevorgyan, *Chem. Rev.* **2007**, *107*, 3117; f) Z. Zhu, Y. Wei, M. Shi, *Chem. Soc. Rev.* **2011**, *40*, 5534; g) I. Marek, S. Simaan, A. Masarwa, *Angew. Chem.* **2007**, *119*, 7508; *Angew. Chem. Int. Ed.* **2007,** 46, 7364; h) F. Miege, C. Meyer, J. Cossy, *Beilstein J. Org. Chem.* **2011**, *7*, 717; i) A. Archambeau, F. Miege, C. Meyer, J. Cossy, *Acc. Chem. Res.* **2015**, *48*, 1021

[2] a) *Carbocyclic Three- and Four-Membered Ring Compounds* (Ed.: A. de Meijere), *Houben-Weyl:* Vol E17d, 2695–2759, Georg Thieme Verlag: Stuttgart, **1996**; b) M. S. Baird, *Science of Synthesis*, **2010**, *47b*, 1111.

[3] For reviews on [2+1]-cycloaddition of alkynes with diazo compounds, see: a) V. Dave, E. W. Warnhoff, *Org. React.* **1970**, *18*, 217; b) M. N. Protopopova, E. A. Shapiro, *Russ. Chem. Rev.* **1989**, *58*, 667.

[4] For recent examples, see: a) J. F. Briones, H. M. L. Davies, *J. Am. Chem. Soc.* **2012**, *134*, 11916; b) M. Uehara, H. Suematsu, Yasutomi, Y.; Katsuki, T. *J. Am. Chem. Soc.* **2011**, *133*, 170; c) T. Goto, K. Takeda, N. Shimada, H. Nambu, M. Anada, M. Shiro, K. Ando, S. Hashimoto, *Angew. Chem.* **2011**. *123*, 6935; *Angew. Chem. Int. Ed.* **2011**, *50*, 6803; d) J. F. Briones, J. Hansei K. I. Hardcastle, J. Autschbach, H. M. L. Davies, *J. Am. Chem. Soc.* **201** *132*, 17211; e) F. Wang, T. Luo, J. Hu, Y. Wang, H. S. Krishnan, P. V. Jog, K. Ganesh, G. K. S. Prakash, G. A. Olah, *Angew. Chem.* **2011**, *123*, 729 *Angew. Chem. Int. Ed.* **2011**, *50*, 7153.

[5] H. G. Köser, G. E. Renzoni, W. T. Borden, *J. Am. Chem. Soc.* **1983,** *10* 6359.

[6] *Diazo Compounds: Properties and Synthesis* (Eds.: M. Regitz, G. Maas Academic Press, Orlando, **1986**.

[7] For reviews, see: a) G. Maas, *Angew. Chem.* **2009**, *121*, 8332; *Angew. Chen Int. Ed.* **2009**, *48*, 8186; b) M. Jia, S. Ma, *Angew. Chem.* **2016**, *128*, 928 *Angew. Chem. Int. Ed.* **2016**, *55*, 9134.

[8] M. W. Majchrzak, M. Bekhazi, I. Tse-Sheepy, J. Warkentin, *J. Org. Chen* **1989**, *54*, 1842.

[9] S. Chuprakov, V. Gevorgyan, *Org. Lett.* **2007,** *9*, 4463.

[10] B. Morandi, E. M. Carreira, *Angew. Chem.* **2010,** *122*, 4390; *Angew. Chen Int. Ed.* **2010,** *49*, 4294.

[11] R. Barroso, A. Jiménez, M. C. Pérez-Aguilar, M. Cabal, C. Valdés, *Chen Commun.* **2016,** *52*, 3677.

[12] For selected reviews, see: a) G. Fang, X. Bi, *Chem. Soc. Rev.* **2015**, 44, 812 b) Q. Zheng, N. Jiao, *Chem. Soc. Rev.* **2016**, 45, 4590. c) *Silver in Organi Chemistry* (Ed.: M. Harmata), Wiley, Hoboken, NJ, **2010**.

[13] J. J. Thompson, H. M. L. Davies, *J. Am. Chem. Soc.* **2007**, 129, 6090.

[14] J. F. Briones, H. M. L. Davies, *Org. Lett.* **2011**, 13, 3984

[15] For examples of our reports on silver catalysis, see: a) J. Liu, Z. Liu, P. Liac L. Zhang, T. Tu, X. Bi, *Angew. Chem.* **2015**, *127*, 10764; *Angew. Chem. Int Ed.* **2015**, *54*, 10618; b) P. Xiao, H. Y. Yuan, J. Q. Liu, X. Bi, J. P. Zhan *ACS Catal.* **2015**, *5*, 6177; c) Z. Liu, J. Liu, L. Zhang, P. Liao, J. Song, X. B *Angew. Chem.* **2014**, *126*, 5409; *Angew. Chem. Int . Ed.* **2014**, *53*, 5305; d) Liu, Z. Fang, Q. Zhang, Q. Liu, X. Bi, *Angew. Chem.* **2013**, *125*, 709 *Angew. Chem. Int. Ed.* **2013**, *52*, 6953; e) J. Liu, Z. Liu, N. Wu, P. Liao, Bi, *Chem. Eur. J.* **2014**, *20*, 2154.

[16] For selected reviews on *N*-tosylhydrazones, see: a) Q. Xiao, Y. Zhang, Wang, *Acc. Chem. Res.* **2013**, *46*, 236; b) Y. Xia, Y. Zhang, J. Wang, *AC Catal.* **2013**, *3*, 2586; c) Z. Shao, H. Zhang, *Chem. Soc. Rev.* **2012**, *41*, 560; J. Barluenga, C. Valdés, *Angew. Chem.* **2011**, *123*, 7626; *Angew. Chem. In Ed.* **2011**, *50*, 7486; e) J. R. Fulton, V. K. Aggarwal, J. de Vicente, *Eur. Org. Chem.* **2005,** 1479.

[17] a) C. Battilocchio, F. Feist, A. Hafner, M. Simon, D. N. Tran, D. M. Allwoo D. C. Blakemore, S. V. Ley, *Nature Chem.* **2016**, *8*, 360; b) J. Barluenga, M Tomás-Gamaza, F. Aznar, C. Valdés, *Nature Chem.* **2009,** *1*, 494.

[18] a) W. R. Bamford, T. S. Stevens, *J. Chem. Soc.* **1952**, 4735; b) H. Tan, I. Houpis, R. Liu, Y. Wang, Z. Chen, *Org. Process Res. Dev.* **2015**, *19*, 1044; c) T. Liu, J. Ma, D. Chao, P. Zhang, Q. Liu, L. Shi, Z. Zhang, G. Zhang, *Chem. Commun.* **2015**, *51*, 12775.

[19] a) Z. Liu, P. Liao, X. Bi, *Chem. Eur. J.* **2014**, *20*, 17277; b) Z. Yang, R. K. Kumar, P. Liao, Z. Liu, X. Li, X. Bi, *Chem. Commun.* **2016**, 52, 5936.

[20] a) D. A. Mundal, K. E. Lutz, R. J. Thomson, *J. Am. Chem. Soc.* **2012**, *134*, 5782; b) A. G. Myers, B. Zheng, *J. Am. Chem. Soc.* **1996**, *118*, 4492.

[21] R. A. Seburg, J. A. Hodges, R. J. McMahon, *Helv. Chim. Acta.* **2009**, *92*, 1626.

[22] H. V. R. Dias, R. G. Browning, S. A. Polach, H. V. K. Diyabalanage, C. J. Lovely, *J. Am. Chem. Soc.* **2003**, *125*, 9270.

[23] a) Q. Xiao, Y. Xia, H. Li, Y. Zhang, J. Wang, *Angew. Chem.* **2011**, *123*, 1146; *Angew. Chem. Int. Ed.* **2011**, *50*, 1114; b) M. L. Hossain, F. Ye, Y. Zhang, J. Wang, *J. Org. Chem.* **2013**, *78*, 1236.

[24] M. F. Semmelhack, S. Ho, D. Cohen, M. Steigerwald, L. M. Lee, A. D. Gilber, W. D. Wulff, R. G. Ball, *J. Am. Chem. Soc.* **1994**, *116*, 7108.

[25] J. Ciabattoni, P. J. Kocienski, *J. Am. Chem. Soc.***1969**, *91*, 6534.

[26] P. Q. Le, J. A. May, *J. Am. Chem. Soc.* **2015**, *137*, 12219.

[27] K. Ye, H. He, W. Liu, L. Dai, G. Helmchen, S. You, *J. Am. Chem. Soc.* **2011**, *133*, 19006.

[28] For examples of silver carbenoids, see: a) A. Caballero, E. Despagnet-Ayoub, M. M. Díaz-Requejo, G. Asensio, M. Etienne, P. J. Pérez, *Science* **2011**, *332*, 835; b) H. Luo, G. Wu, Y. Zhang, J. Wang, *Angew. Chem.* **2015**, *127*, 14711; *Angew. Chem. Int. Ed.* **2015**, *54*, 14503; c) M. W. Hussong, W. T. Hoffmeister, F. Rominger, B. F. Straub, *Angew. Chem.* **2015**, *127*, 10472; *Angew. Chem. Int. Ed.* **2015**, *54*, 10331.

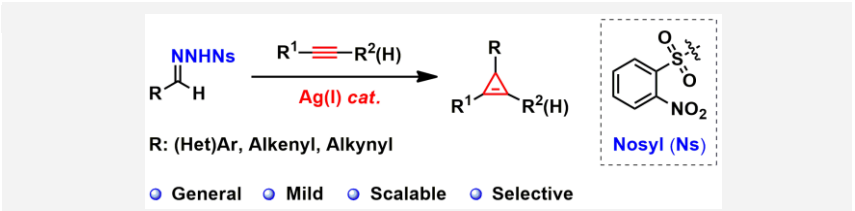
Received: ((will be filled in by the editorial staff))
Revised: ((will be filled in by the editorial staff))
Published online: ((will be filled in by the editorial staff))

10.1002/chem.201605335

Cyclopropenation

*Zhaohong Liu, Qiangqiang Li, Peiqiu Liao, Xihe Bi**
…..…..… Page – Page

Silver-Catalyzed [2+1] Cyclopropenation of Alkynes with Unstable Diazoalkanes: *N*-Nosylhydrazones as Room-Temperature Decomposable Diazo Surrogates



The silver-catalyzed general [2+1] cyclopropenation reaction of alkynes with unstable diazoalkanes has been developed, by for the first time discovering the potential of *N*-nosylhydrazones as room-temperature decomposiable diazo surrogates. This report displayed a powerful synthetic method toward a variety of cyclopropene derivatives that are otherwise difficult to access by conventional methods.