Tetrahedron Letters 55 (2014) 1444-1447

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Bulky, spherical, and fluorinated anion BAr^F induces 'on-water' activity of silver salt for the hydration of terminal alkynes

Sayantani Saha, Abir Sarbajna, Jitendra K. Bera*

Department of Chemistry and Center for Environmental Science and Engineering, Indian Institute of Technology Kanpur, Kanpur 208016, India

ARTICLE INFO

ABSTRACT

Article history: Received 29 October 2013 Revised 12 January 2014 Accepted 13 January 2014 Available online 20 January 2014

Keywords: Alkyne Silver Catalysis Hydration On-water

Water as solvent in organometallic reactions offers valuable prospect in terms of its economic, safety, and environmental considerations.¹ Yet, chemists have long discarded water simply because of its immiscibility with non-polar organic molecules. Breslow introduced the concept of 'on-water' activity to explain unusual rate enhancement of a reaction in water as compared to an organic solvent.² It is now recognized that the improved rate is linked to enhanced interactions between the reagents and the catalyst on the water surface.³ The high surface tension of water favors minimal contact between hydrophobic molecules and water allowing different components to mix efficiently. It is thus felt that metal-based catalysts that are hydrophobic may prove beneficial for 'on-water' organometallic catalysis.

Hydration of alkynes to carbonyl compounds is an important reaction that follows 100% atom efficiency.⁴ Hg(II) salts in aqueous sulfuric acid solution had been the favored catalyst for a long time.⁵ However, toxicity of mercury has furnished this option obsolete. Since then, a variety of metal based catalysts containing Pt,⁶ Ir,⁷ Au,⁸ Rh,⁹ Fe,¹⁰ and Pd¹¹ have been developed. These catalysts display the Markovnikov selectivity and hydrate terminal alkynes to methyl ketones (Scheme 1). Anti-Markovnikov products were obtained at first by Wakatsuki employing Ru catalysts with phosphane ligands.¹² Grotjahn then followed it with the use of a bifunctional catalyst.¹³ A variety of Ru based catalysts have been introduced since then which form aldehydes from alkynes.¹⁴



AgBAr^F displays remarkable 'on-water' activity for catalytic hydration of terminal alkynes although it is

ineffective in common organic solvents. Liquid alkynes do not require additive or co-solvent whereas a

small amount of ethyl acetate triggers quantitative conversions for solid alkynes.

Scheme 1. Silver catalyzed hydration of terminal alkynes.

Ag(I) salts are known to promote Au catalysts for alkyne hydration. Nolan reported a hybrid (NHC)Au¹/AgSbF₆ system for the same at part-per-million catalyst loading.¹⁵ In 1965, Dillar reported catalytic hydration of *N*-propargylamides by using a methanolic solution of AgNO₃.¹⁶ In 1993, Marsella employed AgOTf to selectively hydrate 2-methyl-3-butyn-2-ol.¹⁷ It is only in 2012 that several reports appeared utilizing Ag based catalysts for the hydration of a wide variety of alkynes. Ag(I)-exchanged silicotungstic acid is shown to be an efficient catalyst which works in the absence of organic solvent.¹⁸ The Wagner group revealed that AgSbF₆ selectively hydrates terminal alkynes at 10 mol % catalyst loading in methanol/water (10:1) mixture at 75 °C giving yields greater than 90%.¹⁹ Other solvent mixtures such as tetrahydrofuran/water (10:1) gave considerably lower yield (55%) for 4-phenylbutyne. It was emphasized that although methanol is not essential for the hydration process, its presence clearly improves the reaction rate. In the same year, the Chakraborty group reported similar activity for AgOTf but only in ethyl acetate at 80 °C.²⁰ A host of other organic solvents was found to be not effective. The same reaction in neat water gave less than 10% yield in 24 h. AgBF₄ in acetic acid is recently reported as an efficient catalyst for both terminal and internal alkynes.²¹





© 2014 Elsevier Ltd. All rights reserved.

etrahedror

^{*} Corresponding author. Tel.: +91 5122597336. *E-mail address: jbera@iitk.ac.in* (J.K. Bera).

^{0040-4039/\$ -} see front matter © 2014 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.tetlet.2014.01.045



Scheme 2. Silver tetrakis 3,5-bis(trifluoromethyl)phenyl borate.

 Table 1

 Hydration of phenyl acetylene using different Ag(I) catalysts and solvents^a

Entry	Catalyst	Solvent ^b	Time (h)	Conversion ^c (%)
1	AgSbF ₆ , AgNO ₃ , AgOAc, AgPF ₆ , AgOTf, Ag ₂ O, AgBF ₄ , Ag ₂ CO ₃	H ₂ O	12	<1
2	AgBAr ^F	MeOH/ H ₂ O (10:1)	24	37
3	AgBAr ^F	EtOAc/ H ₂ O (10:1)	24	0
4	AgBAr ^F	H ₂ O	6	86
5	AgBAr ^F	H ₂ O	12	99
6	AgBAr ^F	D_2O	6	50 ^d
7	AgBAr ^F	(H ₂ O) ^e	6	40

 $^{\rm a}$ All reactions were carried out using phenylacetylene (1 mmol), and catalyst (0.1 mmol) at 80 $^{\circ}\text{C}.$

^b Total volume 3 mL.

^c Determined by GC–MS analysis using *n*-dodecane as an internal standard.

^d C₆H₅COCD₃.

^e 1 equiv with respect to alkyne.

The counter-anion of the Ag(1) salts and the solvent medium appears to influence the hydration efficiency. We employed a bulky, spherical, and highly fluorinated anion BAr^F [tetrakis 3,5-bis(tri-fluoromethyl)phenyl borate] (Scheme 2) in an anticipation that the non-coordinating anion would enhance metal Lewis acidity, increase hydrophobicity and thus improve the catalytic efficiency.²² Although AgBAr^F turned out to be ineffective in common organic solvents for alkyne hydration, it showed remarkable activity in neat water. Herein, we report the chemo-selective 'on-water' hydration of a wide range of solid and liquid terminal alkynes catalyzed by AgBAr^F.

Initial exploratory reactions were carried out using phenyl acetylene as a model substrate. All results related to optimization studies are summarized in Table 1. AgNO₃, AgOAc, AgSbF₆, AgPF₆, AgOTf, Ag₂O, AgBF₄, and Ag₂CO₃ (10 mol %) were inactive for the model substrate phenyl acetylene (1 mmol) at 80 °C in neat water (3 mL). AgBAr^F afforded a sluggish conversion in MeOH/H₂O medium (10:1) after 24 h whereas no product could be detected in EtOAc/H₂O. Remarkably, AgBAr^F gave acetophenone in 86% yield in neat water within 6 h and complete conversion occurred after 12 h. The desired product was isolated by simple extraction with ethyl acetate. Switching the solvent to D₂O drastically lowered the yields to 50% in 6 h. D₂O has higher cohesive pressure and viscosity than H₂O which makes mixing of the substrates difficult and thus lowers the rate of product formation.²³ Reaction was also carried out in neat condition with 1 equiv of water with respect to alkyne. Only 65% conversion was recorded after 12 h which is considerably lower compared to quantitative conversion recorded

Ta	ble	2
	~~~	_

AgBAr^F catalyzed hydration of terminal alkynes^a

Entry	Alkyne	Product	Time (h)	Conversion ^b (%)
1			12	>99
2	MeO	MeO	6	>99
3			6	>99
4	Me	Me	12	84
5			12	82
6	Br	Br	12	75
7	N	N	12	70
8	, S S S S S S S S S S S S S S S S S S S	∠, S	12	85
9		_	_	0
10		No	24	48
11	MeO	MeO	12	>99 ^c
12	Ŭ,	<b>N</b>	12	>99 ^c
13	Сно	СНО	12	>99 ^c
14			24	87 ^{c,d}
15			24	62 ^{c,d}
16		$\sim\sim\sim$	24	50 ^{c,d}
17		3a, 3b, 3c	24	48, 30, 10 ^{c,d,e}
18	<_}=-<_>	_	_	0

 $^{\rm a}$  All reactions were carried out using alkynes (1 mmol), catalyst (0.1 mmol), and water (3 mL) at 80 °C.

^b Determined by GC–MS analysis using *n*-dodecane as an internal standard.

 $^{c}~10\,\mu\text{L}$  of EtOAc was added as an additive.

^d Carried out inside a sealed glass tube.

^e See Scheme 4.

in bulk water (3 mL). A control experiment was carried out using KBAr^F. No product was formed in the absence of AgBAr^F confirming that Ag(I) is the critical reagent in this reaction. In situ generated AgBAr^F from 1:1 AgNO₃ and KBAr^F afforded 75% conversion for



Scheme 3. Meyer–Schuster rearrangement.

the model reaction in 6 h that is lower in yields compared to  $AgBAr^{F}$  (86%).

Subsequently, the scope of AgBAr^F was explored under optimized conditions (10 mol % catalyst loading at 80 °C) in neat water (3 mL) with a wide variety of alkynes. Liquid aromatic alkynes were efficiently converted to the corresponding ketones with high conversions. Electron rich aromatic alkynes (Table 2, entries 1-5) showed better conversions in comparison to alkynes that contain electron withdrawing groups (entries 6 and 7). For 4-ethynylbenzonitrile (entry 7), selective hydration occurred for the terminal alkyne whereas the nitrile group remained unaffected. The reaction was extended to alkynes containing heterocyclic rings. No product was observed for 2-ethynylpyridine (entry 9) but high yields (85%) were obtained for 3-ethynylthiophene (entry 8). The lack of reactivity for the pyridine analogue could be attributed to catalyst deactivation via metal coordination to the pyridine nitrogen. In case of 1,3-diethynyl benzene (entry 10), conversion was less (48%) and only mono hydration product was obtained.

For 'on-water' reactions, the hydrophobic reactants form a heterogeneous phase on water surface where transformation takes place. To form a secondary phase, one of the reactants needs to be a liquid. This has been a major hindrance to broaden the scope of 'on-water' reaction. We addressed this issue during the course of this investigation while dealing with solid alkynes. A heterogeneous phase could be attained on water by the addition of a little amount of liquid substance featuring some intrinsic propertiesimmiscible with water, lighter than water, moderately high boiling point, and being inert under the reaction conditions. We screened a large number of organic solvents with solid alkynes among which only ethyl acetate gave the desired results. Addition of  $10 \,\mu L$  of environmentally benign ethyl acetate afforded quantitative conversion in 12 h for solid alkynes (entries 11-13). For propargylic alcohol (Scheme 3), hydration reaction led to the Meyer-Schuster rearrangement product instead of the expected methyl ketones.²⁴ It could be argued at this point that ethyl acetate is the actual solvent and water has no positive effect except being a reagent. It was however discarded since reaction of solid alkyne 1-ethynyl-2,4,5trimethylbenzene in 3 mL of EtOAc/H₂O (10:1) mixture gave only marginal yield (<5%) after 24 h.

We further attempted less reactive aliphatic alkynes under identical conditions but it was not successful. Different additives were added to activate the triple bond including inorganic acid  $H_2SO_4$  and organic tosylic acid but it did not improve the outcome. Addition of  $Et_3N$  to facilitate the formation of silver acetylide, a possible intermediate in this reaction, was also futile. Addition of 10 µL of ethyl acetate did not afford the desired products, but significant conversions were observed when reactions were carried out inside sealed glass tube at 80 °C (entries 14–16). For 1,7-octadiyne (entry 17), conversion was high. Cyclized compounds of monohydrated product were obtained with minor amount of double hydrated 2,7-octadione (Scheme 4). Hydration of internal alkyne was also investigated under both conditions—only water and water +10  $\mu$ L of ethyl acetate. But no product was detected for diphenyl acetylene (entry 18). The fact that internal alkynes do not hydrate under the reaction conditions led us to conclude that the likely mechanism for terminal alkynes involves Ag-acetylide species.

AgBAr^F does not hydrate alkynes in most organic solvents. A possible explanation could be that organic solvents dilute the silver catalyst to such an extent that the reaction becomes impractical. To rule out the possibility of dilution effect, we carried out model reaction in 3 mL of MeOH/H₂O medium (10:1) at different catalyst loadings (20, 30 and 50 mol %). A maximum conversion of 41% was recorded after 24 h. Considering a very similar conversion (37%) at 10 mol % catalyst loading under identical conditions, it can be safely assumed that the lower activity of AgBAr^F in organic solvent is not due to dilution. It is also shown that the use of bulk water (3 mL) leads to higher conversions than when 1:1 alkyne-water mixture was employed. Minimal ion pair interactions in water may be linked to better activity. However, it is not relevant here since AgBAr^F is insoluble in water. The remarkable alkyne-hydration activity of AgBAr^F could only be explained in terms of 'onwater' effect. Catalyst AgBAr^F and liquid alkyne form a hydrophobic secondary phase on the water surface. The enforced hydrophobic interactions that bring together the reagents and the catalyst are responsible for the 'on-water' activity. Clearly, such congregation is favored by bulky, spherical, and fluorinated anion BAr^F where other silver salts fail. For solid alkynes, a small amount of ethyl acetate is needed which dissolves the alkyne and the catalyst to form an oily phase on the water surface. Ethyl acetate also promotes hydration for aliphatic alkynes only under pressured condition. It is postulated that ethyl acetate is hydrolyzed in the presence of bulk water and Ag(I) forming acetic acid, a Brønsted acid that favors the hydration process. This work thus suggests that increase in catalyst hydrophobicity might improve its 'on-water' activity.

# Acknowledgments

This work is financially supported by the Department of Science and Technology (DST), India, and the Council of Scientific and Industrial Research (CSIR) of India. We thank Prof. Y.D. Vankar for useful discussions and Prof. D.H. Dethe for providing one alkyne derivative. J.K.B. thanks DST for the Swarnajayanti fellowship. S.S. thanks CSIR, India, and A.S. thanks UGC, India for fellowships.

## Supplementary data

Supplementary data (full experimental details) associated with this article can be found, in the online version, at http://dx.doi.org/ 10.1016/j.tetlet.2014.01.045.



Scheme 4. Hydration of 1,7-octadiyne.

## **References and notes**

- (a) Dixneuf, P. H.; Cadierno, V. Metal-Catalyzed Reactions in Water; Wiley-VCH: Weinheim, Germany, 2013; (b) Chanda, A.; Fokin, V. V. Chem. Rev. 2009, 109, 725; (c) Cornils, B.; Herrmann, W. A. Aqueous-Phase Organometallic Catalysis: Concepts and Applications; Wiley-VCH Verlag GmbH: Weinheim, 2004.
- (a) Rideout, D. C.; Breslow, R. J. Am. Chem. Soc. 1980, 102, 7816; (b) Narayan, S.; Muldoon, J.; Finn, M. G.; Fokin, V. V.; Kolb, H. C.; Sharpless, K. B. Angew. Chem., Int. Ed. 2005, 44, 3275.
- (a) Zhou, C.; Wang, J.; Li, L.; Wang, R.; Hong, M. Green Chem. 2011, 13, 2100; (b) Hayashi, Y. Angew. Chem., Int. Ed. 2006, 45, 8103; (c) Blackmond, D. G.; Armstrong, A.; Coombe, V.; Wells, A. Angew. Chem., Int. Ed. 2007, 46, 3798; (d) Pirrung, M. C. Chem. Eur. J. 2006, 12, 1312; (e) Jung, Y.; Marcus, R. A. J. Am. Chem. Soc. 2007, 129, 5452; (f) Biffinger, J. C.; Kim, H. W.; DiMagno, S. G. ChemBioChem 2004, 5, 622.
- (a) Otera, J. Modern Carbonyl Chemistry; Wiley-VCH: Weinheim, Germany, 2000. Vol. 103; (b) Bruneau, C.; Dixneuf, P. H. Chem. Commun. 1997, 507; (c) Alonso, F.; Beletskaya, I. P.; Yus, M. Chem. Rev. 2004, 104, 3079; (d) Hintermann, L.; Labonne, A. Synthesis 2007, 1121; (e) Menashe, N.; Reshef, D.; Shvo, Y. J. Org. Chem. 1991, 56, 2912.
- 5. March, J. Advanced Organic Chemistry; Wiley: New York, 1985; p 683.
- (a) Baidossi, W.; Lahav, M.; Blum, J. J. Org. Chem. 1997, 62, 669; (b) Francisco, L. W.; Moreno, D. A.; Atwood, J. D. Organometallics 2001, 20, 4237; (c) Lucey, D. W.; Atwoood, J. D. Organometallics 2002, 21, 2481.
- (a) Kanemitsu, H.; Uehara, K.; Fukuzumi, S.; Ogo, S. J. Am. Chem. Soc. 2008, 130, 17141; (b) Hirabayashi, T.; Okimoto, Y.; Saito, A.; Morita, M.; Sakaguchi, S.; Ishii, Y. Tetrahedron 2006, 62, 2231.
- (a) Gómez-Suárez, A.; Oonishi, Y.; Meiries, S.; Nolan, S. P. Organometallics 2013, 32, 1106; (b) Corma, A.; Ruiz, V. R.; Leyva-Pérez, A.; Sabater, M. J. Adv. Synth. Catal. 2010, 352, 1701; (c) Leyva, A.; Corma, A. J. Org. Chem. 2009, 74, 2067; (d) Casado, R.; Contel, M.; Laguna, M.; Romero, P.; Sanz, S. J. Am. Chem. Soc. 2003, 125, 11925; (e) Mizushima, E.; Sato, K.; Hayashi, T.; Tanaka, M. Angew. Chem., Int. Ed. 2002, 41, 4563; (f) Fukuda, Y.; Utimoto, K. J. Org. Chem. 1991, 56, 3729.

- 9. (a) James, B. R.; Rempel, G. L. J. Am. Chem. Soc. 1969, 91, 863; (b) Blum, J.; Huminer, H.; Alper, H. J. Mol. Catal. 1992, 75, 153.
- (a) Cabrero-Antonino, J. R.; Leyva-Pérez, A.; Corma, A. Chem. Eur. J. 2012, 18, 11107; (b) Wu, X.-F.; Bezier, D.; Darcel, C. Adv. Synth. Catal. 2009, 351, 367; (c) Damiano, J. P.; Postel, M. J. Organomet. Chem. 1996, 522, 303.
- 11. Fukuda, Y.; Shiragami, H.; Uchimoto, K.; Nozaki, H. J. Org. Chem. 1991, 56, 5816.
- 12. Tokunaga, M.; Wakatsuki, Y. Angew. Chem., Int. Ed. 1998, 37, 2867.
- Grotjahn, D. B.; Incarvito, C. D.; Rheingold, A. L. Angew. Chem., Int. Ed. 2001, 40, 3884.
- (a) Tokunaga, M.; Suzuki, T.; Koga, N.; Fukushima, T.; Horiuchi, A.; Wakatsuki, Y. J. Am. Chem. Soc. 2001, 123, 11917; (b) Suzuki, T.; Tokunaga, M.; Wakatsuki, Y. Org. Lett. 2001, 3, 735; (c) Grotjahn, D. B.; Lev, D. A. J. Am. Chem. Soc. 2004, 126, 12232; (d) Chevallier, F.; Breit, B. Angew. Chem., Int. Ed. 2006, 45, 1599; (e) Labonne, A.; Kribber, T.; Hintermann, L. Org. Lett. 2006, 8, 5853; (f) Hintermann, L; Dang, T. T.; Labonne, A.; Kribber, T.; Xiao, L; Naumov, P. Chem. Eur. J. 2009, 15, 7167; (g) Boeck, F.; Kribber, T.; Xiao, L; Hintermann, L. J. Am. Chem. Soc. 2011, 133, 8138.
- 15. Marion, N.; Ramón, R. S.; Nolan, S. P. J. Am. Chem. Soc. 2009, 131, 448.
- 16. Easton, N. R.; Cassady, D. R.; Dillard, R. D. J. Org. Chem. 1965, 30, 3084.
- 17. Meier, I. K.; Marsella, J. A. J. Mol. Catal. 1993, 78, 31.
- 18. Rao, K. T. V.; Prasad, P. S. S.; Lingaiah, N. Green Chem. 2012, 14, 1507.
- 19. Bui, M.; Thuong, T.; Mann, A.; Wagner, A. Chem. Commun. 2012, 434.
- **20.** Das, R.; Chakraborty, D. Appl. Organomet. Chem. **2012**, 26, 722.
- 21. Chen, Z.-W.; Ye, D.-N.; Qian, Y.-P.; Ye, M.; Liu, L.-X. Tetrahedron 2013, 69, 6116.
- (a) Nishida, H.; Takada, N.; Yoshimura, M.; Sonoda, T.; Kobayashi, H. Bull. Chem. Soc. Jpn. **1984**, 57, 2600; (b) Kumar, P. G. A.; Pregosin, P. S. Organometallics **2004**, 23, 5410; (c) Dabb, S. L.; Ho, J. H. H.; Hodgson, R.; Messerle, B. A.; Wagler, J. Dalton Trans. **2009**, 634; (d) Blakenstein, J.; Pfaltz, A. Angew. Chem., Int. Ed. **2001**, 40, 4445; (e) Saha, B.; Ghatak, T.; Sinha, A.; Rahaman, S. M. W.; Bera, J. K. Organometallics **2011**, 30, 2051; (f) Wüstenberg, B.; Pfaltz, A. Adv. Synth. Catal. **2008**, 350, 174; (g) Ho, J. H. H.; Hodgson, R.; Wagler, J.; Messerle, B. A. Dalton Trans. **2010**, 9, 4062.
- 23. Graziano, G. J. Chem. Phys. 2004, 121, 1878.
- 24. Engel, D. A.; Dudley, G. B. Org. Biomol. Chem. 2009, 7, 4149.