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PII: S0040-4039(17)30104-1
DOI: http://dx.doi.org/10.1016/j.tetlet.2017.01.072
Reference: TETL 48575

To appear in: *Tetrahedron Letters*

Received Date: 15 December 2016
Revised Date: 16 January 2017
Accepted Date: 23 January 2017

Please cite this article as: Tanemura, K., Suzuki, T., Hydration of aromatic terminal alkynes catalyzed by sulfonated condensed polynuclear aromatic (S-COPNA) resin in water, *Tetrahedron Letters* (2017), doi: http://dx.doi.org/10.1016/j.tetlet.2017.01.072

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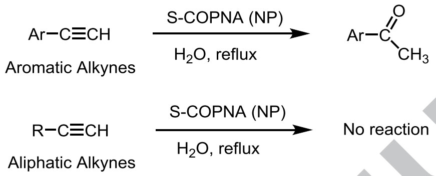

Tetrahedron Letters
journal homepage: www.elsevier.com

Hydration of aromatic terminal alkynes catalyzed by sulfonated condensed polynuclear aromatic (S-COPNA) resin in water

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ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

Keywords:
Hydration
Alkynes
Water
Ketones
Solid acids
Acid catalysts

ABSTRACT

Hydration of aromatic terminal alkynes in the presence of a catalytic amount of sulfonated condensed polynuclear aromatic (S-COPNA) resin in water gave the corresponding methyl ketones in good yields. On the other hand, aliphatic terminal alkynes did not react at all under the employed conditions. Chemoselective hydration of aromatic terminal alkyne in the presence of aliphatic terminal alkyne catalyzed by S-COPNA resin was carried out.

The hydration of alkynes is a synthetically useful and atom economical method for the synthesis of ketones.[1] This transformation is of great importance in industrial purposes as well as in laboratory use. The traditional procedure using a catalytic amount of mercury salts has been known.[2,3] In order to avoid the use of highly toxic mercury salts, many metal catalysts such as Au,[4-6] Ag,[7-9] Pt,[10,11] Ru,[12] Pd,[13] Fe,[14,15] Co,[16] and Ga[17] have been devised. As the method using a Brønsted acid, H_2SO_4-mediated reaction has been reported.[18,19] However, this method requires large amounts (> 1500 equiv) of H_2SO_4.[20] Although the reactions catalyzed by super acids such as TfOH,[20] Tf_2NH,[20] and Nafion NR50[21] have been reported, these reagents are considerably acidic and expensive. Recently, gallic acid/tannic acid-catalyzed hydration has been devised.[22]

Organic transformations catalyzed by hydrophobic polymers in water without the use of harmful organic solvents have been paid for much attention since water is an easily available, safe, economical, and environmentally friendly solvent.[23,24] In addition, organic reactions using polymers are of great interest because they realize easy work-up and recycling of the catalysts.

During the course of our investigations on sulfonated condensed polynuclear aromatic (S-COPNA) resins[25,26] and sulfonated polyarenes,[27,28] we found that S-COPNA (NP) resin (NP = naphthalene) is the quite useful catalyst for the hydration of aromatic terminal alkynes in water. In this paper, we report the results for the transformation of various alkynes catalyzed by S-COPNA (NP) resin in water.

First, we examined the hydration of 4-ethynyltoluene (**3**) in the presence of a catalytic amount of highly hydrophobic S-COPNA (PR) resin (PR = pyrene) or sulfonated polypyrene (S-PPR) at reflux temperature for 16 h in various solvents. The results are shown in Table 1. In dioxane-H_2O (1 : 1) which formed a homogeneous phase, the reactions proceeded more slowly than those in the other biphasic media such as toluene-H_2O and heptane-H_2O in both cases of S-COPNA (PR) resin and S-PPR (entries 2-6).[29] Interestingly, S-COPNA (PR)-catalyzed reaction in water completed within 5 h to give 4-methylacetophenone (**23**) in good yield (entry 1).

Table 1
Acid-catalyzed hydration of alkyne **3** in various solvents[a]

Entry	Solvent	Yield (%)[b]	
		S-COPNA (PR)	S-PPR
1	H_2O	81[c]	37
2	Dioxane - H_2O (1:1)	54	13
3	$n$$Bu_2O$ - H_2O (1:1)	72	80
4	$CHCl_2CHCl_2$ - H_2O (1:1)	80	82
5	Toluene - H_2O (1:1)	82	81
6	Heptane - H_2O (1:1)	72	84

[a] Alkyne **3** (2.0 mmol), catalyst (0.2 mmol), solvent (4 mL), reflux (bath temp. 120 °C), 16 h, 600 rpm.
[b] Isolated yield.
[c] 5 h.

Next, Table 2 summarizes the results for various sulfonated polymers and monomeric Brønsted acids in water. S-COPNA resins were more active than the other sulfonated polymers and monomeric Brønsted acids (entries 1 and 2). The low yields of S-PPR and sulfonated polynaphthalene (S-PNP) would be

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attributed to the considerably high hydrophobic nature of these polymers which were separated from the reaction mixture to attach at the neck of the flask during the reactions. Although Dowex 50WX8 resin worked most efficiently in the employed commercially available sulfonated polymers, it required 60 h to complete the reaction (entry 6). It is noteworthy that the employed sulfonated polymers except S-PPR and S-PNP were superior to monomeric Brønsted acids in water. Although S-COPNA (PR) resin was the most active catalyst, it gradually decomposed and was completely inactive on the fourth recycling (Table 3, entry 1). The elemental analysis of the recovered S-COPNA (PR) resin after the fourth use was $C_{1.000}H_{0.745}O_{0.163}S_{0.012}$ [S-COPNA (PR) resin: $C_{1.000}H_{0.725}O_{0.396}S_{0.088}$]. The acid density of S-COPNA (PR) resin decreased from 4.02 to 0.76 mmol·g^{-1}, indicating the removal of the sulfo group. The IR spectra showed the desulfonation[16] from aromatic rings of S-COPNA (PR) resin. The intensity of the characteristic absorptions at 1168 and 1029 cm^{-1} assigned to OH vibration of the sulfo groups largely decreased and the absorptions due to the phenolic OH groups did not appear. Although S-COPNA (NP) resin is less active than S-COPNA (PR) resin, it did not lose the activity after the fifth recycling (Table 3, entry 2).

Table 2

Hydration of alkyne **3** catalyzed by various acids in water[a]

Entry	Catalyst	Acid density (mmol·g^{-1})	Yield (%)[b]
1	S-COPNA (PR)	4.02	81[c]
2	S-COPNA (NP)	3.42	84 (51)[d] (35)[e]
3	S-PPR	2.25	30
4	S-PNP	2.05	22
5	Amberlyst 15	4.8	43
6	Dowex 50WX8	4.8	59 (80)[f]
7	Nafion NR50	0.9	51
8	H_2SO_4	-	6
9	TsOH	-	16
10	TfOH	-	10
11	$C_8F_{17}SO_3H$	-	32

[a] Alkyne **3** (2.0 mmol), catalyst (0.2 mmol H^+), H_2O (4 mL), reflux (bath temp. 120 °C), 8 h, 600 rpm.
[b] Isolated yield.
[c] 5 h.
[d] In dioxane – H_2O (1 : 1) (4 mL).
[e] In toluene – H_2O (1 : 1) (4 mL).
[f] 60 h.

Table 3

Recycle experiments for the hydration of alkyne **3**

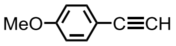
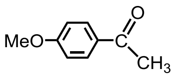
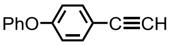
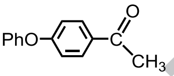
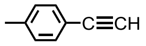
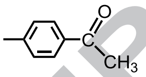
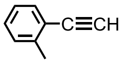
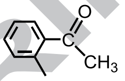
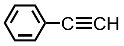
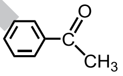
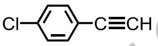
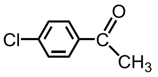
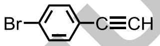
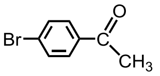
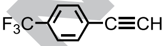
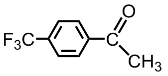
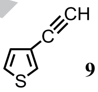
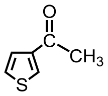
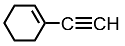
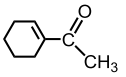
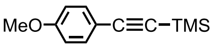
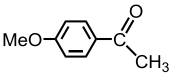
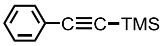
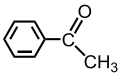
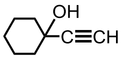
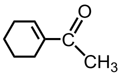
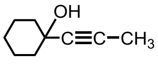
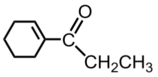
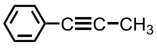
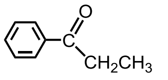
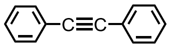
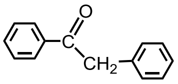
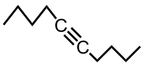
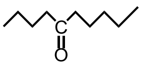
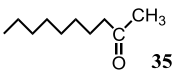
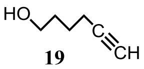
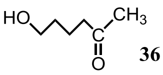
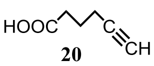
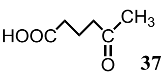
Entry	Catalyst	Yield (%)[a]				
		1st	2nd	3rd	4th	5th
1[b]	S-COPNA (PR)	81	41	16	0	0
2[c]	S-COPNA (NP)	82	82	84	80	80

[a] Isolated yield.
[b] Alkyne **3** (2.0 mmol), S-COPNA (PR) (0.2 mmol), H_2O (4 mL), reflux (bath temp. 120 °C), 5 h, 600 rpm.
[c] Alkyne **3** (2.0 mmol), S-COPNA (NP) (0.2 mmol), H_2O (4 mL), reflux (bath temp. 120 °C), 8 h, 600 rpm.

Table 4 shows the results for the reactions of a wide range of alkynes catalyzed by S-COPNA (NP) resin in water. Aromatic terminal alkynes except **8** were transformed to the corresponding methyl ketones in good to excellent yields, respectively (entries

Table 4

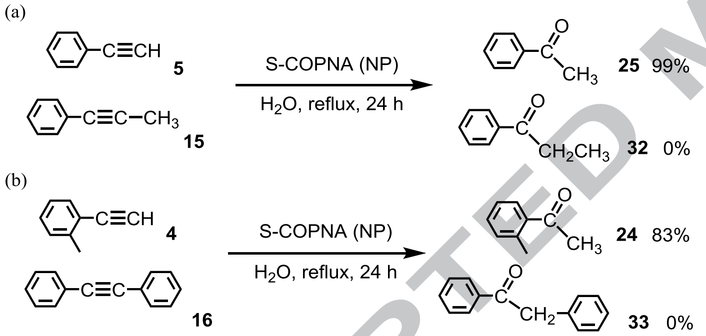
Hydration of various alkynes catalyzed by S-COPNA (NP)[a]

Entry	Alkyne	Time (h)	Product	Yield (%)[b]
1	 **1**	3	 **21**	90
2	 **2**	16	 **22**	96
3	 **3**	8	 **23**	84
4	 **4**	24	 **24**	82
5	 **5**	24	 **25**	96[c]
6	 **6**	72	 **26**	89[d]
7	 **7**	72	 **27**	82[d]
8	 **8**	72	 **28**	0[d]
9	 **9**	8	 **29**	87
10	 **10**	8	 **30**	99[c]
11	 **11**	24	 **21**	92
12	 **12**	72	 **25**	94[c]
13	 **13**	24	 **30**	81[c]
14	 **14**	8	 **31**	75
15	 **15**	72	 **32**	35[d]
16	 **16**	72	 **33**	0[d]
17	 **17**	72	 **34**	0[d]
18	 **18**	72	 **35**	0[d]
19	 **19**	72	 **36**	0[d]
20	 **20**	72	 **37**	0[d]

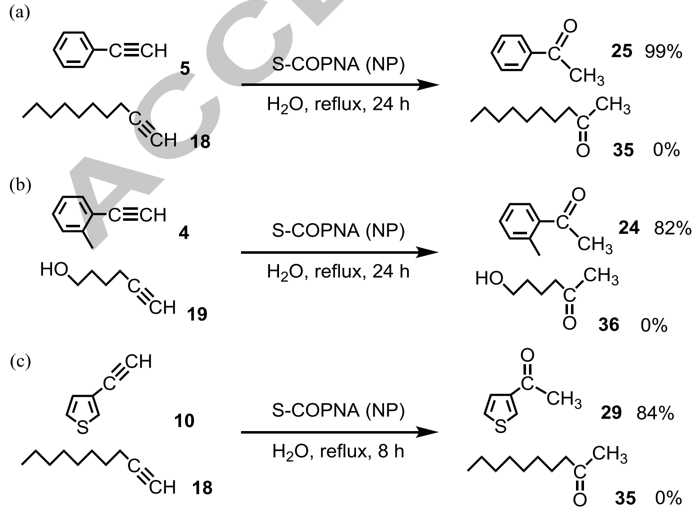
[a] Alkyne (2.0 mmol), S-COPNA (NP) (59 mg, 0.2 mmol), H_2O (4 mL), reflux (bath temp. 120 ℃), 600 rpm.
[b] Isolated yield.
[c] Yield was determined by ^{1}H-NMR with anisole as the internal standard.
[d] 0.4 mmol of S-COPNA (NP) was used.

1-7 and 9). The hydration of **6** and **7** possessing electron-withdrawing halogen groups in the phenyl moiety proceeded slowly to afford **26** and **27** in good yields, respectively. The presence of the strongly electron-withdrawing trifluoromethyl group suppressed the reaction entirely (entry 8). α,β-Unsaturated alkyne **10** tolerated the reaction conditions without decomposition to give **30** in excellent yield. Aryl trimethylsilyl (TMS) acetylenes, which can be easily synthesized from Sonogashira coupling,[30,31] reacted to give the corresponding methyl ketones more slowly than the unprotected alkynes *via* the deprotection followed by hydration (entries 11 and 12).[32] Further utility of S-COPNA (NP) resin was explored on the reactions of propargylic alcohols **13** and **14**, which were converted into α,β-unsaturated ketones **30** and **31** *via* the dehydration followed by the hydration of the alkyne, respectively (Rupe rearrangement).[33] The reaction of internal alkyne, 1-phenyl-1-propyne (**15**) underwent quite slowly to afford carbonyl compound **32**. No reaction occurred with aromatic internal alkyne **16** and aliphatic internal alkyne **17**. It is noteworthy that aliphatic terminal alkynes **18**-**20** were inert under the employed conditions.

Based on the difference in reactivities between aromatic terminal alkynes and aromatic internal alkynes, we explored the chemoselective hydration of **4** and **5**. Aromatic terminal alkyne was hydrated exclusively in the presence of aromatic internal alkyne to give the corresponding methyl ketone in good yield (Scheme 1). We also succeeded the chemoselective hydration of aromatic terminal alkyne in the presence of aliphatic terminal alkyne (Scheme 2). This is the first example as far as we know which resulted in the exclusive reaction of aromatic terminal alkyne in the presence of aliphatic terminal alkyne.



Scheme 1. Chemoselective hydration of aromatic terminal alkyne in the presence of aromatic internal alkyne.



Scheme 2. Chemoselective hydration of aromatic terminal alkyne in the presence of aliphatic terminal alkyne.

Table 5 summarizes the results for the competitive hydration between aromatic terminal alkyne **3** and aliphatic terminal alkyne **18** promoted by metal catalysts and Brønsted acids. In the cases of examined metal-catalyzed reactions, both compounds **23** and **35** were obtained in moderate to good yields (entries 1-6). Because the rates of the hydration of **3** and **18** did not have large differences, it was difficult to obtain **23** in good yields without the production of **35**. Exclusive hydration of **3** was observed when super acids as well as S-COPNA (NP) resin were employed as the catalysts (entries 7-10). It was found to be a general tendency of Brønsted acid catalysis. The hydration catalyzed by Nafion NR50 in AcOH progressed faster than that in water (Table 2, entry 7 and Table 5, entry 9), but a large amount of alkaline solution is required to remove AcOH on work-up. It should be noted that S-COPNA (NP) resin realized the chemoselective hydration of **3** in the presence of **18** which was difficult to carry out by the metal catalysts (entry 10).

Table 5
Competitive hydration of alkynes **3** and **18** by various catalysts

Entry	Catalyst	Yield (%)[a]	
		23	**35**
1[b]	$HgSO_4$	84	74
2[c]	AuCl	91	99
3[d]	$[(Ph_3P)AuCH_3]$	83	85
4[e]	$AgSbF_6$	58	80
5[f]	AgOTf	98	67
6[g]	$[PtCl_2(C_2H_4)]_2$	43	92
7[h]	Tf_2NH	87	4
8[h]	TfOH	90	0
9[i]	Nafion NR50	88	0
10[j]	S-COPNA (NP)	84	0

[a] Isolated yield.
[b] Alkyne **3** (2.0 mmol), Alkyne **18** (2.0 mmol), $HgSO_4$ (0.11 mmol), H_2O (1 mL), H_2SO_4 (0.04 mL), 90 °C, 12 h.
[c] Alkyne **3** (2.0 mmol), Alkyne **18** (2.0 mmol), AuCl (0.1 mmol), MeOH (4 mL), H_2O (8 mmol), 65 °C, 1 h, N_2.
[d] Alkyne **3** (10.0 mmol), Alkyne **18** (10.0 mmol), $[(Ph_3P)AuCH_3]$ (0.01 mmol), MeOH (5 mL), H_2O (0.5 mL), TfOH (0.25 mmol), 70 °C, 0.5 h.
[e] Alkyne **3** (2.0 mmol), Alkyne **18** (2.0 mmol), $AgSbF_6$ (0.2 mmol), MeOH (3 mL), H_2O (0.3 mL), 75 °C, 48 h.
[f] Alkyne **3** (2.0 mmol), Alkyne **18** (2.0 mmol), AgOTf (0.2 mmol), EtOAc (6 mL), H_2O (0.4 mL), 80 °C, 48 h.
[g] Alkyne **3** (2.0 mmol), Alkyne **18** (2.0 mmol), Zeise's dimer (0.014 mmol), THF (1.5 mL), H_2O (6 mmol), 70 °C, 48 h.
[h] Alkyne **3** (2.0 mmol), Alkyne **18** (2.0 mmol), Tf_2NH or TfOH (0.2 mmol), dioxane (4 mL), H_2O (6 mmol), 100 °C, 5 h.
[I] Alkyne **3** (5.0 mmol), Alkyne **18** (5.0 mmol), Nafion NR50 (167 mg, 0.15 mmol), AcOH (2 mL), H_2O (15 mmol), 100 °C, 3 h.
[j] Alkyne **3** (2.0 mmol), Alkyne **18** (2.0 mmol), S-COPNA (NP) (59 mg, 0.2 mmol), H_2O (4 mL), 120 °C, 12 h.

In summary, we devised an environmentary benign method for the hydration of aromatic terminal alkynes in water. It constitutes a useful procedure for selective hydration of aromatic terminal alkyne in the presence of aliphatic terminal alkyne. In addition, it is noteworthy that (1) the work-up procedure is remarkably simple because S-COPNA (NP) resin is a solid acid and (2) S-COPNA (NP) resin can be reused without significant loss of activity.

Acknowledgments

We thank the Division of Chemical Analysis, Systems Engineering for the elemental analyses. We thank the Research Promotion Grant (NDU Grants N-16010) from Nippon Dental University.

Supplementary data

Supplementary data (general experimental procedures, data of IR and ^{1}H-NMR spectra of the products) associated with this article can be found, in the online version.

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* Hydration of aromatic terminal alkyne in the presence of aliphatic terminal alkyne.

* The solvent is environmentally friendly water.

* The work-up procedure is remarkably simple.

* The catalyst can be recycled without significant loss of activity.