

Mixed Surfactant Nano-Assemblies for Allylic Alcohol Etherification in Aqueous Medium

Waqar Ahmed,^{*,[a]} Hyun Sung Lee,^[a] and Pil Seok Chae^{*,[a]}

Mixed nano-assemblies formed by two surfactants have rarely been used to catalyze organic reactions. In this study, nano-assemblies formed by SDS and CTAB were applied for the etherification of allylic alcohols with benzyl, aliphatic, and natural product alcohols at room temperature in an aqueous medium. In the presence of SDS-CTAB nano-assemblies and Brønsted acid catalyst *p*TSA, various allylic alcohols were reacted with different nonallylic alcohols to generate the desired ether products in moderate to good yields (62%–93%). SDS-CTAB nano-assemblies provide hydrophobic environments that effectively encapsulate both allylic alcohols and benzyl/aliphatic alcohols in their

interiors. The anionic surface charge of these assemblies not only facilitates proton transfer from *p*TSA in the bulk solution to the allylic alcohol within the assemblies, but also stabilizes the allylic carbocation intermediates and localizes them on the surface. As a result, the reaction of allylic alcohols with nonallylic alcohols in the SDS-CTAB nano-assemblies increased both reaction rate and synthetic yields of the desired products by effectively suppressing two side reactions: reduction and self-etherification. This methodology provides an environmentally friendly approach for obtaining various allylic ether products.

1. Introduction

A great deal of effort has been made to functionalize allylic compounds including allylic alcohols.^[1] Allylic alcohols have been functionalized through the formation of C–C, C–O, and C–N bonds.^[2] Allylic alcohols substituted with aryl rings tend to form highly stable carbocation upon removal of OH-group, facilitated by the presence of Brønsted acids.^[3] These carbocation intermediates can then be functionalized using various nucleophiles.^[4] One main side reaction associated with the nucleophilic functionalization of allylic alcohols is reduction, particularly in the presence of reducing agents. For example, allylic alcohols have been observed to undergo reduction to form the corresponding methylene product in the presence of methyl alcohol (a reducing agent), along with palladium and titanium oxide (TiO₂) as transition metal catalysts and *para*-toluenesulfonic acid (*p*TSA) as an acid additive under photo-irradiation conditions.^[5] The reduction of 1,3-diarylprop-2-en-1-ol has also been reported in the presence of transition metals, LiPF₆ and Brønsted acids, and isopropanol or 4-methylbenzyl alcohol as a reductant.^[6] There are a few reports on the etherification of 1,3-diarylprop-2-en-1-ol with benzyl alcohol. For example, Radtanajiravong and coworkers employed 1,3-diphenylprop-3-en-1-ol with benzyl alcohol to generate the allyl–benzyl ether product in the presence of phytic acid in toluene, along with

the amination of these allylic alcohols.^[7] Varala and coworkers developed a method for the etherification of allylic alcohol with various aliphatic alcohols in the presence of molecular iodine (I₂) using organic solvents, such as alcohol or acetonitrile.^[8] Barbero and coworkers used a reusable Brønsted acid catalyst, *o*-benzenedisulfonimide, for the etherification of allylic alcohol with aliphatic or benzyl alcohols using tetrahydrofuran as a solvent.^[9] However, there is little research on the etherification of allylic alcohols in aqueous solutions.^[10]

Organic reactions in water have immense importance due to the environmentally friendly nature of this solvent. The rate and selectivity of organic reactions were often enhanced when carried out in water due to the instability of nonpolar organic reactants in the polar water medium.^[11] However, most organic reactions in aqueous environments suffer from low synthetic yields, primarily due to the limited solubility of organic reactants in water. Amphiphilic self-assemblies, including micelles and vesicles, have been extensively used to facilitate organic reactions in water by increasing the solubility of organic reagents.^[11a,12] These nano-assemblies-mediated reactions include C–C,^[13] C–O,^[14] and C–N^[12c,15] bond formation, including amination, cyclization, condensations,^[16] ester hydrolysis,^[17] ester formation,^[18] and multicomponent reactions.^[19] Surfactants used to generate nano-assemblies are typically either negatively charged amphiphilic compounds [e.g., sodium dodecyl sulfate (SDS), sodium octyl sulfate (SOS), and sodium dodecylbenzene sulfonate (SDBS)] or nonionic amphiphiles [e.g., tocopheryl polyethylene glycol succinate (TPGS) and Triton-X 100].^[16] In addition, nano-assemblies formed from two amphiphilic components have been rarely applied to organic reactions, although these mixed nano-assemblies have been widely used in other fields, such as drug delivery^[20] and gene delivery.^[21] The presence of two amphiphilic components in nano-assemblies (i.e., mixed nano-assemblies)^[12f–h] can

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provide distinct physical properties and effects compared to single component nano-assemblies. For example, assemblies formed from SDS and CTAB have shown significant variations in hydrodynamic diameter, critical micelle concentration (CMC) and other physical properties depending on their relative concentrations.^[22] Arpan et al. demonstrated that mixing SDS and CTAB solutions below their CMC values results in an Ostwald ripening effect, which is highly time-dependent in terms of the size and other physicochemical properties of the assemblies.^[23] Although these mixed assembly systems have been studied extensively for their physicochemical studies, they have scarcely been explored as catalytic systems for organic reactions. A few examples include the use of mixed nano-assemblies of cationic/anionic surfactants with nonionic surfactants for the oxidation of alcohols using Cr(VI) or Ag(III)periodate and the dephosphorylation of diethyl 2,4-dinitrophenyl phosphate (DEDNPP) in aqueous medium.^[24] The mixed micelle assemblies have also been employed to investigate their effects on hydrolysis reactions.^[25] The hydrolysis rates of phenyl benzoate, phenyl salicylate, and phthalimide were examined in mixed micelle assemblies formed by [C₁₆E₂₀]_T (Brij-58) and CTAB in an alkaline medium.^[26,27] Additionally, mixed micelle assemblies of fluorocarbon/hydrocarbon surfactants were used to study the hydrolysis rate of phenyl trifluoroacetate.^[28] These studies demonstrated that, in addition to surfactant concentration, the polarity of assembly interfaces and substrate encapsulation efficiency influence the reaction rate. The reaction of *t*-butylhydroquinone with 4-hexadecylbenzenediazonium was studied in the mixed micelle assembly formed by CTAB and hexaethylene glycol monododecyl ether (C₁₂E₆).^[29] This study revealed that the system was biphasic and the reaction rate depended on the micellar composition. Mixed micelle assemblies have also been applied for enzymatic reactions involving various enzymes, including peroxidases, dehydrogenases, glycosidases, polymerases, α -chymotrypsin, and lipases.^[30]

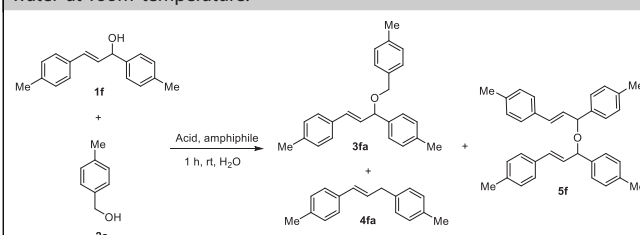
In the present study, we developed a method for the etherification of various allylic alcohols with several benzylic or aliphatic alcohols in water, attained by catalytic nano-assemblies formed from anionic SDS and cationic CTAB. Despite the challenge of achieving dehydration reactions in water due to their reversible nature, SDS-CTAB nano-assemblies provided good-to-excellent reaction yields of ether-functionalized products with diverse substrates. This study represents the first example of the etherification of allylic alcohols with various non-allylic alcohols in an aqueous solution, achieved using mixed nano-assemblies formed by SDS and CTAB amphiphiles.

2. Results and Discussion

2.1. Optimization of Reaction Conditions

We began with the reaction of 1,3-bis(4-tolueyl)-prop-2-en-1-ol (**1f**) with 4-methylbenzyl alcohol (**2a**) in the presence of trifluoroacetic acid (TFA) and SDS used as Brønsted acid and as

Table 1. Optimization of reaction conditions of allylic etherification in water at room temperature.^{a)}



Entry	Amphiphile	Acid	Yield (%) ^{b)} 3fa/4fa/5f
1	SDS	TFA	10/0/25
2	SDS	HCl	20/24/10
3	SDS	TfOH	Trace/51/0
4	SDS	<i>p</i> TSA	29/10/12
5	SDBS	<i>p</i> TSA	21/12/18
6	SOS	<i>p</i> TSA	17/trace/13
7	CTAB	<i>p</i> TSA	16/28/13
8	SDS:CTAB (1:0.05)	<i>p</i> TSA	48/30/0
9	SDS: CTAB (1:0.1)	<i>p</i> TSA	47/33/0
10	SDS: CTAB (1:0.25)	<i>p</i> TSA	58/20/0
11	SDS: CTAB (1:0.5)	<i>p</i> TSA	65/12/0
12	SDS: CTAB (1:1)	<i>p</i> TSA	48/21/10
13	CTAB:SDS (1:0.05)	<i>p</i> TSA	18/21/15
14	CTAB:SDS (1:0.1)	<i>p</i> TSA	21/19/18
15	CTAB:SDS (1:0.25)	<i>p</i> TSA	39/28/12
16	CTAB:SDS (1:0.5)	<i>p</i> TSA	43/24/10
17 ^{c)}	SDS:CTAB (1:0.5)	<i>p</i> TSA	73/trace/0

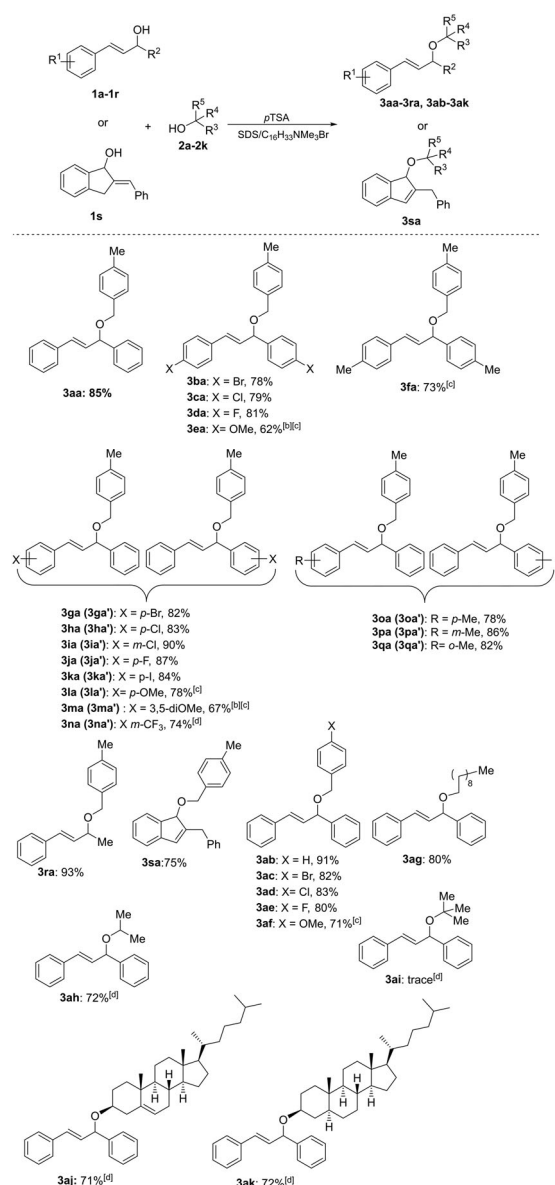
a) Reaction conditions: **1f** (0.2 mmol), **2a** (0.4 mmol), acid (0.03 mmol), amphiphile (0.02 mmol), water (0.4 mL), rt, 1 h. ^{b)} Isolated yield. ^{c)} 45 min.

surfactant catalysts in water, respectively (Table 1). The desired product **3fa** was obtained in only 10% yield, while the self-condensed product **5f** obtained in 25% yield (entry 1). The use of other Brønsted acids such as hydrochloric acid (HCl), trifluoromethane sulfonic acid (TfOH), and *para*-toluenesulfonic acid (*p*TSA) resulted in a marginal increase of **3fa** (HCl = 20% and *p*TSA = 29%) or a complete loss of the product (TfOH = trace) (entry 2–4). Interestingly, the use of TfOH led to the formation of only the reduced side product (**4fa**) under the conditions, likely due to the high acidity of this acid. When various surfactants were tested, none of SOS, SDBS, and CTAB enhanced the yield of the desired product **3fa** (16%–21%) (entry 5–7), suggesting the anionic or cationic surfactants alone are not effective for product formation. We hypothesized that mixed assemblies of cationic and anionic surfactants could resolve the issues associated with using only one type of surfactant. Therefore, we applied mixed assemblies formed by both SDS (major) and CTAB (minor) for the etherification reaction of **1f**, increasing the equivalency of CTAB from 0.05 to 1.0 (entries 8–12). The yield of **3fa** increased steadily as the CTAB amount increased from 0 (29%) to 0.5 equivalent (65%), but a further increase in CTAB to 1.0 equivalent reduced the product yield to 48%. The

improvement in yield was due to the decreased formation of the reduced side product **4fa** (12%) and the complete suppression of the self-condensed product **5f** (0%) (entry 8–12). When cationic assemblies formed by CTAB (major) and SDS (minor) were used, the formation of **3fa** was suboptimal, with substantial amounts of the two side products [**4fa** (19%–28%) and **5f** (10%–18%)] being obtained. Under these conditions, increasing the amount of SDS in these cationic assemblies tended to improve the synthetic yields. Specifically, the yield of **3fa** increased from 18% to 43% as the amount of SDS increased from 0.05 to 0.5 equiv. in the CTAB assemblies (entries 13–16). These results indicate that mixed nano-assemblies formed by two surfactant components (SDS and CTAB) are superior to SDS-only or CTAB-only assemblies in the etherification of allylic alcohol with benzyl alcohol. Anionic assemblies formed from SDS (major) and CTAB (minor) were more effective for this reaction than cationic assemblies formed from CTAB (major) and SDS (minor). Previous studies have shown that allyl–benzyl ethers, like the product **3fa**, tend to reduce into allyl aryl compounds, like **4fa**, in the presence of Brønsted acid.^[6a,d] Because of this conversion, extending the reaction time can be unfavorable for formation of the desired product, **3fa**. By reducing the reaction time from 1 h to 45 min, we observed an enhanced yield of **3fa** (73%), along with suppressed formation of the undesired side product **4fa** under the same conditions (entry 17).

2.2. Substrate Scope of Allylic Alcohol Etherification

We applied the optimized reaction conditions to a variety of allylic alcohols (**1a–1s**) and benzylic, and aliphatic alcohols (**2a–2k**) as shown in Scheme 1. When reacted with **2a**, 1,3-diphenylprop-2-en-1-ol (**1a**), and its symmetrically substituted variants with halides (**1b–1d**), methoxy (**1e**), or methyl (**1f**) at the *para*-positions of both phenyl rings afforded products **3aa** (85%), **3ba** (78%), **3ca** (79%), **3da** (81%), **3ea** (62%), and **3fa** (73%). The allyl alcohol (**1e**) substituted with electron-rich benzene rings provided a relatively low yield, presumably due to the high tendency of the desired product (**3ea**) to convert into the side product (**4ea**, 18%) under the reaction conditions. Use of various unsymmetrical allylic alcohols (**1g–1n**), where one phenyl ring of the two was substituted with halide (F/Cl/Br/I), methoxy, or CF₃, provided the corresponding products in an isomeric mixture (**3ga–3na** and **3ga'–3na'**) with yields ranging from 67% to 90%. The formation of the isomeric mixture originates from the resonance structure of the allylic carbocation intermediate generated by the dehydration of the allylic alcohols. The allylic alcohols with a methoxy substituent on one phenyl ring (**1l** and **1m**) reacted faster with **2a**, decreasing the reaction time to 45 min. In the case of electron-rich allylic alcohol (**1m**), which has two methoxy groups on the phenyl ring, the reduced side product **4ma** was obtained in 8% yield, along with the desired product (**3ma**), resulting in a reduced synthetic yield (67%). Similarly, *ortho*, *meta*-, and *para*-methyl substituted unsymmetrical allylic alcohols (**1o–1q**) provided isomeric mixtures of **3oa–3qa** and **3oa'–3qa'** in good yields (78%–86%). These results indicate that biaryl allylic alcohols with various electron-donating or electron-



Scheme 1. Substrate scope study using different allylic alcohols (**1a–1s**) and benzyl/aliphatic alcohols (**2a–2k**). **Reaction conditions:** an allylic alcohol (**1a–1s**, 0.2 mmol), benzyl/aliphatic alcohol (**2a–2k**, 0.4 mmol), *p*TSA (0.03 mmol), SDS/CTAB (0.02/0.01 mmol, 2:1 in 0.4 mL water), 12 h at rt under Ar. [a] Isolated yield. [b] Side product [**4ea** (18%) or **4ma** (8%)]. [c] 45 min. [d] 55 °C.

withdrawing substituents on either or both aromatic groups are compatible with the etherification reaction with benzyl alcohol (**2a**). In contrast to the previous examples, unsymmetrical allylic alcohols with 4-phenyl-but-3-en-2-ol (**1r**) and (*E*)-2-benzylidene-2,3-dihydro-1H-inden-1-ol (**1s**) provided the single isomers (**3ra** (93%) and **3sa** (75%)), respectively. The single isomer formation of **3ra** is likely due to the marked difference in stability between two resonance structures of the allyl carbocation intermediate. Interestingly, reactant **1s** underwent migration of double bond from the exocyclic to the endocyclic position during the etherification reaction, originating from double bond isomerization of the allylic carbocation intermediate.

Next, we carried out the reaction of 1,3-diphenylprop-2-en-1-ol (**1a**) with various benzyl alcohols with no substituent (**2b**), or a substituent of bromine (**2c**), chlorine (**2d**), fluorine (**2e**), or methoxyl (**2f**) to investigate their compatibility with the etherification of allylic alcohols. These benzyl alcohols provided good yields of the products: **3ab** (91%), **3ac** (82%), **3ad** (83%), **3ae** (80%), and **3af** (71%, in 45 min). Aliphatic alcohols such as 1-decanol (**2g**) and isopropanol (**2h**) were well-incorporated into the corresponding products (**3ag** (80%) and **3ah** (72%)).

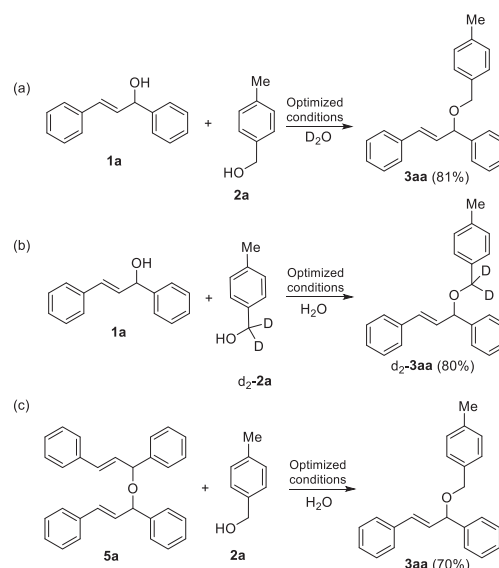
In the case of isopropanol, increasing the reaction temperature from 20 °C to 55 °C enhanced the synthetic yield of the product from 61% to 72%, presumably due to the improved solubility and reactivity of this alcohol in water. However, the optimal reaction conditions failed to convert sterically hindered *tert*-butanol (**2i**) into the desired product **3ai** in a reasonable yield even at 55 °C.

A trace amount of the product was obtained in a mixture with a substantial amount of the side product **5ai** (See ¹H NMR spectrum in the ESI). Along with steric hindrance, the susceptibility of this tertiary alcohol to dehydration under the acidic conditions is likely responsible for its failure to react with allylic alcohol. Consequently, **1a** underwent self-etherification to give side product **5ai**.

Based on this result, it is expected that primary and secondary alcohols, but not tertiary alcohols, are effective at affording the desired products when reacting with allylic alcohols under the conditions. To further test this, we employed two natural products bearing secondary alcohol groups, cholesterol (**2j**) and β -cholestanol (**2k**), for reactions with the allylic alcohol (**1a**) at 55 °C. Gratifyingly, these natural products underwent smooth etherification with the allylic alcohol, providing the products **3aj** (71%) and **3ak** (72%), respectively. Thus, this methodology enables to modification of these natural products to transform them into functional molecules for various applications.^[31]

2.3. Control Experiments

A series of control experiments were conducted to gain insight into the reaction mechanism (Scheme 2). The reaction of allylic alcohol **1a** with 4-methylbenzyl alcohol (**2a**) in D₂O under the optimized conditions yielded the product (**3aa**) in 81% yield, indicating that water is not directly involved in the reaction mechanism (Scheme 2a). When the reaction of **1a** was conducted with deuterated 4-methylbenzyl alcohol (*d*₂-**2a**), *d*₂-**3aa** was obtained in 80% yield, implying that no H-D scrambling occurred (Scheme 2b). Finally, when bis(1,3-diphenylprop-2-en-1-yl) ether **5a** was employed with 4-methylbenzyl alcohol (**2a**) under the optimized conditions, the product **3aa** was obtained in 70% yield. This result indicates that the self-etherized side product (e.g., **5a**) can be converted into the desired product in the presence of benzyl alcohol (Scheme 2c). This finding suggests that the self-etherized dimeric products of allylic alcohols can be unsymmetrically cleaved to generate the allylic carbocation intermediate, which then reacts with benzyl alcohol derivatives to form the desired products.



Scheme 2. Control experiments for investigation of the reaction mechanism. (a) Reaction of the allylic alcohol (**1a**) with 4-methylbenzyl alcohol (**2a**) in D₂O or (b) deuterated 4-methylbenzyl alcohol (*d*₂-**2a**) in H₂O, and (c) reaction of an ether of **5a** with 4-methylbenzyl alcohol (**2a**). The reactions were conducted under optimized conditions.

Table 2. Hydrodynamic diameters (*D*_h) and zeta-potential (ζ -potential) values of SDS-CTAB nano-assemblies in the absence/presence of *p*-TSA and/or two reactants (**1f** and **2a**) in water at room temperature.

Entry	Composition	<i>D</i> _h (nm)	ζ -Potential (mV)
1	SDS	6.0	−77.2
2	SDS:CTAB (1:0.05)	818	−75.3
3	SDS: CTAB (1:0.1)	777	−69.2
4	SDS: CTAB (1:0.25)	611	−65.3
5	SDS: CTAB (1:0.5)	250	−55.3
6	SDS: CTAB (1:1)	139	−2.8
7	SDS: CTAB (1:0.5) + <i>p</i> TSA	246	−42.5
8	SDS: CTAB (1:0.5) + <i>p</i> TSA + 1f + 2a	526	−41.4

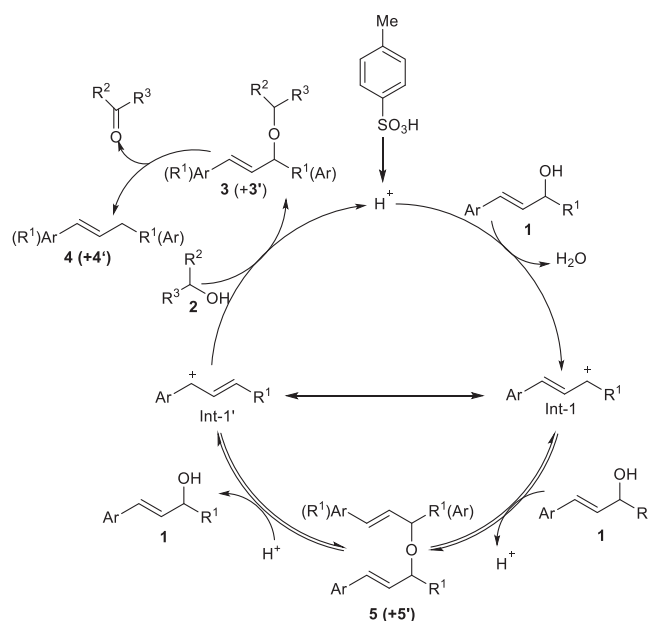
2.4. Characterization of Nano-Assemblies Formed by SDS and CTAB

The etherification reactions of allylic alcohols were conducted in mixed nano-assemblies formed by the anionic surfactant (SDS) and cationic surfactant (CTAB), with the optimal feed ratio of these two surfactants for product formation found to be 1:0.5. To explore the role of nano-assemblies in the current reaction, we characterized these SDS-CTAB assemblies in terms of size and zeta (ζ) potential. The size and ζ -potential of SDS-CTAB assemblies were measured using dynamic light scattering (DLS) and the results are summarized in Table 2. Assemblies formed by SDS alone have a hydrodynamic diameter (*D*_h) of 6.0 nm, which is consistent with the reported value of 4.4 nm.^[32] Upon addition of 0.05 equivalent of CTAB, the assembly size increased dramatically from 6.0 nm and 818 nm. Further additions of CTAB led to a gradual decrease in assembly size; 777 nm (0.1 equiv. CTAB), 611 nm (0.25 equiv. CTAB), 250 nm (0.5 equiv.

CTAB), and 139 nm (1.0 equiv. CTAB). The addition of *p*TSA into the SDS and CTAB (1: 0.5) solution had little effect on the size of the assemblies, but upon the inclusion of the starting materials (**1f** and **2a**), the assembly size increased from 246 to 526 nm (Table 2 and Figure S1). This enlargement of assemblies is likely due to the incorporation of these two reactions within their hydrophobic interiors. As this assembly size yielded the best synthetic results under the given conditions, the small vesicular architecture with a large surface area appears to be responsible for an effective reaction.^[33] Similarly, variations in the size of CTAB assemblies were also measured with the addition of SDS (Table S1 and Figure S2). The results showed that CTAB assemblies tend to increase in size with increasing SDS content.

To investigate the surface charge of the assemblies, we measured the ζ -potential as a function of the SDS-CTAB ratio. As expected from the negative charge, assemblies formed by SDS alone exhibited a highly negative ζ -potential (−77.2 mV). Upon the addition of CTAB in increasing amounts from 0.05 to 0.5 equivalent, the ζ -potential of the assemblies gradually decreased, reaching −55.2 mV with 0.5 equivalent CTAB (Table 2 and Figure S2b). When 1.0 equivalent CTAB was added to SDS assemblies, a dramatic decline in ζ -potential to −2.8 mV was observed (Figure S2b). Upon addition of *p*TSA to the SDS-CTAB (1:0.5) assemblies, a slight decrease in ζ -potential from −55.3 mV to −42.5 mV was observed, presumably due to partial protonation of SDS. Further additions of starting materials (**1f** and **2a**) to the [SDS-CTAB (1:0.5) + *p*TSA] assemblies resulted in minimal change in ζ -potential (−41.4 mV), consistent with the neutral nature of these reactants.

The negative surface charge of the SDS-CTAB assemblies plays a crucial role in the etherification of allylic alcohols with benzylic/aliphatic alcohols. We conceive that, due to the negative charge of the assemblies, protons are effectively transferred from *p*TSA in bulk water to allylic alcohol incorporated within the nano-assemblies, leading to dehydration of allylic alcohols and formation of the allyl carbocation intermediate. The negative charge of assembly surfaces can also stabilize the cationic carbocation intermediate, thereby increasing reaction rate.^[34] Localization of the stabilized allyl carbocation intermediates at the assembly surfaces promotes the etherification reaction with benzyl or aliphatic alcohols. The polar alcohol groups of these alcohols are oriented toward the surface of assemblies, while the hydrophobic benzene ring or alkyl chain resides in the interiors of the assemblies. Therefore, the localization of the allyl carbocation intermediates on the assembly surface, coupled with the orientation of benzyl or aliphatic alcohols in the assembly interiors, significantly increases their effective molarity, thus enhancing the reaction. In addition to surface charge, the size of mixed nano-assemblies play an important role in the etherification of allylic alcohols. Thus, the current results underscore the critical role of the size and surface charge of SDS-CTAB assemblies in the etherification of allylic alcohols with various primary and secondary alcohols. A similar trend was also found in an alcohol oxidation reaction.^[35]



Scheme 3. Plausible mechanism of etherification of allylic alcohol **1** with alcohol **2**. Compound **3** is a desired product while compounds **4** and **5** are two side products of this reaction.

2.5. Proposed Reaction Mechanism of Allylic Alcohol Etherification

Based on previous results,^[6a,c,d] control experiments (Scheme 2), and the physical properties of SDS-CTAB assemblies (Table 2), we propose the reaction mechanism (Scheme 3). The protons of *p*TSA in the bulk water are transferred to the allylic alcohols within the interiors of the SDS-CTAB assemblies, facilitated by the negative surface charge of the assemblies. After protonation, the allylic alcohol (**1**) undergoes dehydration to form a resonance-stabilized allylic carbocation intermediate (Int-1 and Int-1'). The sulfate group the SDS, presumably, stabilized this allyl carbocation and circumvent the side reactions associated with it. This intermediate can react with benzyl/aliphatic alcohol (**2**) to yield the desired product (**3** and **3'**). Alternatively, this intermediate may react with unreacted allylic alcohol (**1**) to form the self-etherified products (**5** and **5'**). These side products can revert to Int-1 (Int-1') via heterolytic cleavage under the acidic conditions, thereby contributing to the formation of the desired product (**3**). The proton generated during the product formation can re-enter the catalytic cycle for another etherification reaction. Product **3** could also be reduced into the side product **4** due to the presence of benzyl or isopropyl alcohol, which can act as a reductant. This side reaction was particularly problematic when the aryl groups of allyl or benzyl alcohols are substituted with an electron-donating group (e.g., −OMe) at the *para*-position, leading to a reduced synthetic yield.

3. Conclusion

In summary, we have developed the efficient method for the etherification of allylic alcohols with various benzylic or

aliphatic alcohols in water, using anionic assemblies formed by SDS and CTAB as nano-reactors. These nano-assemblies proved highly effective at catalyzing the etherification while preventing the formation of reduced side products in the presence of benzylic alcohols. The reaction exhibited a broad substrate scope, accommodating various functional groups on the aromatic rings of allylic alcohols (such as halides, methoxy, methyl, and CF₃) as well as on benzylic alcohols (including halides, methyl, and methoxy groups). Additionally, aliphatic alcohols like decanol and isopropanol, as well as natural products such as 5-cholesten-3 β -ol and β -cholestanol, were successfully converted into the desired products with good yields. These results demonstrate that this methodology is a useful and environmentally friendly approach for the preparation of diverse allylic ether compounds.

Supporting Information

The authors have cited additional references within the Supporting Information.^[36]

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the [Supporting Information](#) of this article.

Keywords: Allylic alcohols · Benzyl alcohols · Brønsted acid · Etherification · Nano-assembly

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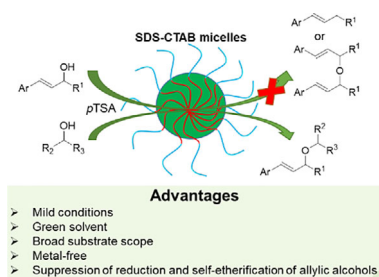
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RESEARCH ARTICLE

The etherification of various allylic alcohols was achieved with a diverse range of benzylic or aliphatic alcohols by utilizing anionic nano-assemblies formed by SDS and CTAB in water at ambient conditions under metal-free conditions. The undesired side reactions of allylic alcohols—reduction and self-etherification—were effectively suppressed under the conditions due to the presence of SDS-CTAB nano-assemblies, thus providing good-to-excellent yields of the various ether products.



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Mixed Surfactant Nano-Assemblies for Allylic Alcohol Etherification in Aqueous Medium