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Pronounced Catalytic Effect of a Micellar Solution of Sodium Dodecylsulfate (SDS) Upon a Three-Component Reaction of Aldehydes, Amines, and Ketones Under Neutral Conditions

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Dedicated to Professor Habib Firouzabadi on the occasion of his 65th birthday

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A micellar solution of anionic, cationic or neutral surfactants can be used as an excellent medium for three-component Mannich reactions of aldehydes, amines, and ketones at room temperature. Sodium dodecylsulfate turned out to efficiently catalyze the reaction in neutral pure water (pH \approx 7), and the corresponding desired β -amino ketones precipitate while the reactions proceedes. This method provides a novel and improved modification of the three-component Mannich

Introduction

Water is a desirable solvent for reasons of cost, safety, and environmental impact. Moreover, environmental consciousness imposes the use of water for organic processes from both industrial and academic viewpoints.^[1-3] Water has unique physical and chemical properties, and its use could enhance the reactivity and selectivity generally achieved in classical organic solvents.^[4] However, organic solvents are still used instead of water for mainly two reasons. First, most organic substrates are not soluble in water, and as a result, water cannot function as a reaction medium. Second, many reactive substrates, reagents, and catalysts are sensitive towards water and decompose or become deactivated in aqueous media. A possible way to improve the solubility of substrates is to use surface-active reagents that can form micelles^[5] or vesicular structures. The use of micellar and vesicle-forming surfactants as catalysts has been investigated in detail for different reactions in aqueous solutions.^[6,7] However, widespread studies in this area are still needed from both the academic and industrial points of view.

The Mannich and related reactions are among the most important C–C-bond-forming reactions in organic synthe-

reaction in terms of mild reaction conditions, clean reaction profile, improved yields, and excellent regio- and diastereoselectivities with a simple workup. Interesting examples of click chemistry under neutral conditions in water were observed.

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sis.^[8] They provide β -amino carbonyl compounds, which are important synthetic intermediates for various pharmaceuticals and natural products.^[9] The increasing popularity of the Mannich reaction has been fueled by the ubiquitous nature of nitrogen-containing compounds in drugs and natural products.^[10] Owing to the importance of β-amino carbonyl compounds, numerous methods for the synthesis of these compounds either by indirect-type or direct-type Mannich reactions have been reported over the years.^[11,12] The main catalysts reported include Lewis acids such as metal triflates^[8f,8g,11c,11f] and chlorides^[8h] and Brønsted^[8d,8e,8i,8j,11a,11d,11e,11g] and heteropoly acids.^[11h] However, when ketones rather than their silvl enolates forms are used directly, Brønsted and Lewis acids require long reaction times and are not effective catalysts. Additionally, in all previous cases, organic solvent was used as a reaction medium (co-solvent) and/or for reaction workup. Consequently, these do not represent green protocols. Additionally, vigorous stirring was required for the success of these reactions due to the poor solubility of the aldehydes, ketones and amines in water. To solve this problem, surfactants were added to form colloidal dispersions as the reaction media. The use of surfactants not only disperses organic substrates in water, but can also make organic synthesis possible inside substrate-containing particles in water.^[12] In the course of our investigations to develop new synthetic reactions in water, we recently have successfully applied the micellar solution of sodium dodecylsulfate (SDS) to the hetero-Michael reaction under neutral conditions and pre-



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pared sulfoxides by the green oxidation of sulfides in aqueous hydrogen peroxide.^[13] Herein, we report a mild, simple, efficient, and regio- and stereoselective method for the preparation of β -amino carbonyl compounds by the Mannich reaction of ketones with aromatic aldehydes and amines (the click Mannich reaction) in the presence of SDS in pure water under neutral conditions.

Results and Discussion

In order to optimize the reaction conditions with respect to the reaction medium, temperature, time, and the mole ratio of the substrates and catalyst, we first studied the three-component reaction of benzaldehyde (2 mmol), aniline (2 mmol) and acetophenone (2 mmol) as a model reaction at room temperature in neutral and acidic water (Table 1, Entries 1 and 2). The reaction proceeded sluggishly, and after a prolonged reaction time (24 h), the corresponding Mannich product was produced in 20% and 25%, respectively. The problem with the use of water in the reaction (this reaction in water as we have observed) was the formation of a gummy mass in the reaction medium as presented in Figure 1. To solve this problem, we performed a similar reaction in micellar media using SDS and sodium dodecyl benzenesulfate (SDBS) as anionic micelles, cetyltrimethylammonium bromide (CTAB), and tetrabutylammonium bromide (TBAB) as cationic micelles and Triton X-100 as a neutral micelle (Table 1, Entries 3–7). We observed a drastic rate enhancement when performing this reaction in water in the presence of 2.5 mol-% of SDS at its critical micelle concentration (CMC) of 3 to produce the desired Michael adduct in 96% yield after 6 h. A similar reaction in the presence of other micellar media (SDBS, CTAB, TBAB, and Triton X-100) did not proceed to completion even after 24 h, and the desired adduct was produced in 85%, 55%, 20%, and 50% yields, respectively, together with

imine and unreacted starting materials. With the aim of improving the reaction time, we added catalytic amounts of a Brønsted acid or Brønsted base to the reaction mixture in order to facilitate the formation of an enol from acetophenone. In these cases, we observed that the Brønsted acid or Brønsted base was not necessarily effective; we observed no improvement with the combination of SDS and HCl,

Table 1. Optimization of reaction conditions.[a]



Entry	Solvent	Catalyst (mol-%)	Time [h]	Yield [%]
1	H_2O	—	24	20
2	H_2O	HCl (5)	24	25
3	H_2O	SDBS (2.5)	24	85
4	H_2O	CTMAB (2.5)	24	55
5	H_2O	TBAB (2.5)	24	20
6	H_2O	Triton X100 (2.5)	24	50
7	$H_2O^{[b]}$	SDS (2.5)	6	96
8	H_2O	SDS (2.5)/HCl (2.5)	5	85
9	H_2O	SDS (2.5)/HClO ₄ (2.5)	5	87
10	H_2O	SDS (2.5)/NaOH (2.5)	6	90
11	CH ₃ CN	SDS (2.5)	24	5
12	CH_2Cl_2	SDS (2.5)	24	5
13	EtOH	SDS (2.5)	24	8
14	solvent-free	SDS (2.5)	24	15

[a] Reaction conditions: solvent (2 mL), room temperature, benzaldehyde (2 mmol), aniline (2 mmol), acetophenone (2 mmol). [b] Under neutral conditions (pH \approx 7).



Figure 1. Left: The function of SDS micellar droplets and hydrogen bonding is shown for Mannich reactions in pure water (the broken lines show hydrogen bonds). Right: Photograph of the reaction of acetophenone with benzaldehyde and aniline in an SDS micellar medium (left) and in pure water (right) after 6 h. In the micellar medium (left), the lower layer is the pure precipitated product and the upper layer is the SDS micellar solution.



Table 2. Micellar solutions of SDS-catalyzed direct Mannich reactions of various aryl aldehydes and aromatic amines with acetophenones.



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Table 2. (continued.)



[a] All the products were fully characterized by the usual spectroscopic techniques. [b] Isolated yields.

 $HClO_4$, or NaOH (Table 1, Entries 8–10). Furthermore, we studied a similar reaction under solvent-free conditions and in organic solvents such as dichloromethane, acetonitrile, and ethanol at room temperature in the presence of SDS. We noticed that SDS in these solvents cannot efficiently catalyze the reaction, and the corresponding Mannich product was produced in less than 15% yield after 24 h (Table 1, Entries 11–14).

According to the obtained results, the catalytic effect of micellar SDS in the Mannich reaction can be explained as follows. Aldehydes, amines, and enolizable ketones, which are expected to produce β -amino ketones, are hydrophobic molecules in aqueous media. In the micellar solution of SDS, the hydrophobic moieties escape from water molecules, which encircle the micelle core of SDS. However, they are activated by hydrogen bonding and are pushed by water molecules into the hydrophobic core of the micellar droplets, where the reactions take place more easily. Water is also a sufficiently polar medium to shift the keto-enol equilibrium to the enol form, which are highly hydrophilic species whose formation is the rate-determining step. This explanation is also schematically presented by Figure 1.

As shown in Figure 1, when the reaction was complete, we added water (4 mL) to the reaction mixture and filtered off and washed with water the precipitated Mannich product to yield the pure 1,3-diphenyl-3-phenylamino-1-propanone in 96% yield. This simple workup opened the door to an entirely green, highly efficient, one-pot Mannich reaction in water.

After this success, in order to ascertain the generality and scope of this one-pot Mannich reaction, we observed the reaction of various amines with aldehydes and acetophenones bearing electron-withdrawing and electron-donating groups proceed smoothly to give the corresponding β - amino carbonyl compounds in excellent yields (Table 2). In the case of amines having electron-donating groups, we obtained the corresponding amino ketones in good yields. Amines with electron-withdrawing groups, such as 4-chloroaniline, 4-cyanoaniline, and 3-nitroaniline also gave the desired products in good yields (Table 2, Entries 4–7). However, under these reaction conditions, aldehydes such as cinnamaldehyde and 4-nitrobenzaldehyde failed to give the Mannich products (data not shown).

The high yield, simple reaction protocol, and originality of this process prompted us to use cyclic and linear aliphatic ketones under these conditions (Table 3). Thus, we carried out the three-component coupling reactions with cyclohexanone (2.5 mmol), aromatic aldehydes (2 mmol), and aromatic amines (2 mmol) at room temperature in water in the presence of 5 mol-% of SDS. The corresponding Mannich products precipitated as the reaction progressed.

After the consumption of the imines (by the fast in situ formation from aldehydes and amines) we added water (4 mL) to the reaction mixture and isolated the desired products by simple filtration without the formation of any side products. We obtained the expected products in moderate yields under these neutral micellar conditions. As the results show (see Tables 2 and 3), cyclohexanone was more reactive than acetophenone because its enol formation was much faster, and therefore, the Mannich reactions proceeded faster.

Interestingly, on the basis of the ¹H and ¹³C NMR, the Mannich reaction exhibited excellent *anti* selectivity under these conditions except for the reaction of 2-nitrobenzalde-hyde, aniline, and cyclohexanone. However, reactions in the presence of other catalysts in water or organic solvents showed lower stereoselectivity (Table 4).

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Table 3. Micellar solutions of SDS-catalyzed direct Mannich reactions of various aryl aldehydes, aromatic amines and cyclohexanone.



[a] All the products were fully characterized by the usual spectroscopic techniques. [b] The *syn/anti* ratio was determined by 1 H and 13 C NMR spectroscopy.

We determined the diastereoselectivity of the reactions by ¹H and ¹³C NMR spectroscopy and by comparing our data with that of known compounds reported in the literature.^[8,11] We also performed the reaction of cyclohexanone with benzaldehyde and aniline in an acidic SDS micellar medium to promote the stereoselectivity. The results show the Brønsted acid enhanced the reaction rate but did not increase the stereoselectivity. The results are tabulated and compared with the other catalysts recently reported in Table 4. The reaction of 2-heptanone as an aliphatic unsymmetrical ketone with benzaldehyde and aniline proceeded in a short reaction time with excellent regioselectivity and in high yield (45 min, 91%). It indicates that the reaction took place at the less-substituted carbon (Scheme 1).

In order to show the merit of the protocol for the Mannich reaction, we compared the results obtained using micellar solutions of SDS with some of those recently reported in the literature for the reaction of acetophenone, aniline, and benzaldehyde, as tabulated in Table 5. Table 4. Investigation of diastereoselectivity of the reaction in acidic and neutral micellar SDS solution, compared with recently reported data.



Entry	Solvent	Catalyst [mol-%]	Time [min]	Yield [%]	synlanti ^[a]	Ref.
1	H ₂ O	SDS (5)/HCl (4.6)	10	85	35:65	_
2	H_2O	SDS (5)/HCl (2.3)	15	86	23:77	_
3	H_2O	SDS (5)/HCl (1.2)	30	92	16:84	_
4	H_2O	SDS (5)	45	93	4:96	-
5	H_2O	H ₃ PW ₁₂ O ₄₀ (0.12)	960	84	37:63	[11h]
6	H_2O	DBSA ^[b] (1)	60	81	26:74	[12b]
7	H_2O	GFQAS ^[c] (0.2)/TsOH (10)	240	83	44:56	[12c]
8	H_2O	Bi(OTf) ₃ ·4H ₂ O (5)	420	84	14:86	[8f]
9	EtOH	BDMS ^[d] (10)	15	86	2:98	[8e]

[a] The *synlanti* ratio was determined by ¹H and ¹³C NMR spectroscopy. [b] Dodecylbenzenesulfonic acid. [c] Quaternary ammonium salt gemini surfactants. [d] Bromodimethylsulfonium bromide.



Scheme 1. Regioselective, three-component, Mannich reaction of 2heptanone, aniline and benzaldehyde in an SDS micellar medium at room temperature.

Table 5. Comparison of the catalytic activity of SDS with those of different catalysts for the Mannich reaction of benzaldehyde, aniline, and acetophenone.

Entry	Solvent	Catalyst	Time [h]	Yield [%]	Ref.
1	PhCH ₃ /C ₆ F ₅ CF ₃	Yb(OPf) ₃	12	98	[8g]
2	EtOH	Silica/sulfuric acid	12	92	[8j]
3	EtOH	NbCl ₅	12	95	[8h]
4	EtOH	HCl	10	81	[8i]
5	H_2O	PS-SO ₃ H	24	75	[11e]
5	H_2O	NaBArF ₄	48	81	[12d]
6	H_2O	$H_{3}PW_{12}O_{40}$	18	76	[11h]
7	H_2O	FQAS/TsOH	12	70	[12c]
8	H ₂ O	SDS	6	96	_

Conclusions

In conclusion, this procedure offers several advantages for the Mannich reaction such as using water as a green solvent, low loadings of cheap and commercially available SDS as a catalyst, neutral conditions (suitable for acid- and base-sensitive substrates), high yields, excellent regio- and stereoselectivity, and clean reactions. In addition, product isolation is easily accomplished by simple filtration, as the products are insoluble in water. This simple work-up is of practical importance, especially for large-scale operations.

Experimental Section

General Procedure for the Mannich Reaction: To a solution of SDS (0.02 M, critical micelle concentration: 3.0) in H_2O (2.0 mL) were added an amine (2 mmol), an aldehyde (2.0 mmol), and acetophenone (2.0 mmol, 0.24 g) or cyclohexanone (2.5 mmol, 0.25 g) successively at room temperature. The mixture was stirred (800 rpm) at the same temperature for the period of time listed in Tables 2 and 3. Water (4 mL) was added to the reaction mixture, and the precipitated Mannich base was separated with a simple filtration. The filtered solid was washed with H_2O and dried to afford the pure products in good to excellent yields. 10 mmol-scale reactions were also carried out without any difficulties. For example, the reaction of benzaldehyde (10 mmol, 1.06 g), aniline (10 mmol, 0.93 g), and acetophenone (10 mmol, 1.20 g) in the presence of 2.5 mol-% of SDS afforded the product in 96% isolated yield after 6 h.

4-(3-Oxo-1,3-diphenylpropylamino)benzonitrile (1g): Yield 90%, white solid, m.p. 151–152 °C. ¹H NMR (250 MHz, CDCl₃): δ = 3.48 (d, *J* = 6.2 Hz, 2 H), 5.04 (s, 1 H), 5.27 (br., 1 H), 6.52 (d, *J* = 8.5 Hz, 2 H), 7.22–7.59 (m, 10 H), 7.86 (d, *J* = 8.5 Hz, 2 H) ppm. ¹³C NMR (62.9 MHz, CDCl₃): δ = 45.8, 54.1, 99.2, 113.2, 120.4, 126.2, 127.8, 128.2, 128.8, 129.0, 133.5, 133.7, 136.4, 141.5, 150.2, 197.8 ppm. (KBr): \tilde{v} = 3388, 2223, 1670 cm⁻¹. C₂₂H₁₈N₂O (326.39): calcd. C 80.96, H 5.56; found C 80.85, H 5.53.

1-(4-Methoxyphenyl)-3-phenyl-3-(phenylamino)propan-1-one (1i): Yield 92%, white solid, m.p. 123–125 °C. ¹H NMR (250 MHz, CDCl₃): δ = 3.32 (dd, J = 15.8, J = 7.5 Hz, 1 H), 3.43 (dd, J = 15.8, J = 5.2 Hz, 1 H), 3.82 (s, 3 H), 4.96 (dd, J = 7.5, J = 5.2 Hz, 1 H), 6.54 (dd, J = 7.7, J = 0.77 Hz, 2 H), 6.64 (td, J = 7.7, J = 0.73 Hz, 1 H), 6.88 (dd, J = 8.6, J = 0.54 Hz, 2 H), 7.06 (t, J = 7.7 Hz, 2 H), 7.03–7.09 (m, 3 H), 7.27–7.30 (m, 2 H), 7.42 (d, J = 7.35 Hz, 2 H), 7.87 (d, J = 8.3 Hz, 2 H) ppm. ¹³C NMR (62.9, CDCl₃): δ = 46.0, 55.0, 55.5, 113.8, 117.7, 122.0, 126.4, 127.3, 128.8, 128.9, 129.1, 130.4, 143.1, 147.1, 163.8, 196.8 ppm. IR (KBr): \tilde{v} = 3382, 1659 cm⁻¹. C₂₂H₂₁NO₂ (331.41): calcd. C 79.73, H 6.39; found C 79.64, H 6.42.

2-[(2-Nitrophenyl)(phenylamino)methyl]cyclohexanone (2b) as a *synlanti* **Mixture:** Yield 91%, light yellow solid. ¹H NMR (250 MHz, CDCl₃): δ = 1.54–2.99 (m, 8 H), 4.45 (br., NH, 0.4 H), 5.22 (d, *J* = 3.3 Hz, 0.68 H), 5.5 (br., NH, 0.6 H), 5.61 (d, *J* = 4.42 Hz, 0.42 H), 6.49–6.56 (m, 2 H), 6.62–6.66 (m, 1 H), 7.03–7.10 (m, 2 H), 7.32–7.50 (m, 2 H), 7.70–7.94 (m, 2 H) ppm. ¹³C NMR (62.9 MHz, CDCl₃): δ = 25.0, 25.1, 27.3, 28.1, 28.4, 33.8, 42.3, 43.3, 52.0, 54.5, 55.4, 56.0, 113.2, 113.9, 117.8, 118.3, 124.8, 125.1, 127.9, 128.6, 129.1, 129.3, 130.0, 130.1, 133.1, 133.3, 137.3, 137.9 146.6, 149.8, 210.2, 213.3 ppm. IR (KBr): \tilde{v} = 3386, 1698 cm⁻¹. C₁₉H₂₀N₂O₃ (324.37): calcd. C 70.35, H 6.21; found C 70.43, H 6.22.

1-Phenyl-1-(phenylamino)octan-3-one (3): Yield 91%, light yellow solid, m.p. 71–73 °C. ¹H NMR (250 MHz, CDCl₃): δ = 0.83 (t, *J* = 6.7 Hz, 2 H), 1.13–1.25 (m, 4 H), 1.45–1.50 (m, 2 H), 2.30 (t, *J* = 7.3 Hz, 2 H), 2.88 (d, *J* = 6.4 Hz, 2 H), 4.53 (br., NH, 1 H), 4.82 (t, *J* = 6.4 Hz, 1 H), 6.52–6.55 (m, 2 H), 6.65–6.65 (m, 1 H), 7.05–7.11 (m, 2 H), 7.21–7.37 (m, 5 H) ppm. ¹³C NMR (62.9 MHz, CDCl₃): δ = 13.4, 22.0, 22.6, 30.8, 43.3, 49.8, 54.0, 113.3, 117.3, 125.8, 126.9, 128.3, 128.7, 142.2, 146.4, 209.3 ppm. IR (KBr): \tilde{v} = 3375, 1701 cm⁻¹. C₂₀H₂₅NO (295.42): calcd. C 81.31, H 8.53; found C 81.15, H 8.51.

Supporting Information (see also the footnote on the first page of this article): ¹H and ¹³C NMR spectra of products.

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