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Copper(II) Triflate–Sodium Dodecyl Sulfate Catalyzed Preparation of 1,2-Diphenyl-2,3-dihydro-4-pyridones in Aqueous Acidic Medium

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Abstract: The reactions between *N*-benzylideneanilines and Danishefsky's diene proceed smoothly in acidic aqueous medium in the presence of a catalytic amount of copper(II) triflate–sodium dodecyl sulfate [Cu(OTf)₂–SDS] to afford the corresponding 1,2-diphenyl-2,3-dihydro-4-pyridones in excellent yields of 84–95%. The aqueous solution containing the catalyst is recovered and reused without any loss in efficiency.

Key words: aza-Diels–Alder reaction, Lewis acid, aqueous medium, pyridones, copper(II) triflate

The 2,3-dihydro-4-pyridone moiety is a versatile building block in organic synthesis as the presence of both enone and amine functionalities allows it to be used either as a donor or acceptor partner in fundamental organic transformations.¹ The stereochemical features of this structure are also interesting: in order to minimize the allylic 1,3-strain, the C-2 substituent is forced to adopt an axial position resulting in the molecule having a distorted shape.² Such deformation is responsible for the high selectivity observed in 1,2- and 1,4-additions and consequent alkylation at the C-3 position. These features make 2,3-dihydro-4-pyridones suitable precursors for the synthesis of alkaloids and aza-sugars.³

Water has proven to be an efficient and green solvent for various organic transformations, and often has successfully enabled processes that cannot be performed in organic media.⁴ In fact, thanks to its peculiar properties and structure (e.g., pH control, H-bonding ability), water may represent an ideal reaction medium for achieving the optimum efficiency in many synthetic processes.

On the other hand, Lewis acid–surfactant–combined catalysts (LASCs) are able to promote several organic transformations; these catalytic systems furnish a hydrophobic molecular environment that favors the approach of reactants. Lewis acid–surfactant–combined catalysts have been successfully employed in Diels–Alder, Mannich and allylation reactions, as well as in nucleophilic ringopening reactions of epoxides and aldol additions.⁵

SYNTHESIS 2012, 44, 2181–2184 Advanced online publication: 25.05.2012 DOI: 10.1055/s-0031-1291040; Art ID: SS-2012-C0282-ST © Georg Thieme Verlag Stuttgart · New York The reaction between *N*-benzylideneanilines **1** and Danishefsky's diene (**2**) is classified as an aza-Diels–Alder cycloaddition reaction (Scheme 1). Due to its importance, this particular transformation has been studied by employing a variety of experimental conditions including the use of acids to promote the reaction in different organic media,⁶ under solvent-free conditions,⁷ and also in water.⁸



Scheme 1 Synthesis of 1,2-diphenyl-2,3-dihydro-4-pyridones **3a–i** via the reaction of *N*-benzylideneanilines **1a–i** and Danishefsky's diene (**2**)

The role of the pH of the aqueous medium⁹ on the efficiency of such transformations and on the use of Lewis acid–surfactant–combined catalysts such as copper(II) tri-flate–sodium dodecyl sulfate [Cu(OTf)₂–SDS] has not been investigated.

Taking into account our previous experience on Lewis catalysis in aqueous media^{4e,f,10} we have investigated the preparation of 1,2-diphenyl-2,3-dihydro-4-pyridones **3a–i** via the reactions of *N*-benzylideneanilines **1a–i** and Danishefsky's diene (**2**) in water, catalyzed by Lewis acids under neutral (pH 7.0) and acidic (pH 4.0) conditions (Scheme 1).

The aza-Diels–Alder reaction between *N*-benzylideneaniline (1a) and Danishefsky's diene (2) was chosen as a model system. Equimolar amounts of substrates were used and the reactions were performed at pH 7.0 or pH 4.0, at a temperature of 30 °C. The results obtained after a reaction time of 10 minutes are summarized in Table 1.

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In aqueous medium under neutral conditions the reaction between **1a** and diene **2** led to formation of only traces of the reaction product **3a** (<2%) being detected (Table 1, entry 1). In the presence of sodium dodecyl sulfate (SDS) (1 mol%), after 10 minutes, the conversion of **1a** into 2,3-dihydro-4-pyridone **3a** was good, but still not complete (Table 1, entry 2).

 Table 1
 Optimization of the Conditions for the Aza-Diels–Alder Reaction between N-Benzylideneaniline (1a) and Diene 2

	Me ₃ SiC	OMe H ₂ O 30 °C, 10 min	
	a 	2 Catalyst	3a
Entry	рн	Catalyst	Conv. (%)
1	7.0	-	<2
2	7.0	SDS	65
3	7.0	Cu(OTf) ₂	85
4	7.0	CoCl ₂	20
5	7.0	NiCl ₂	15
6	7.0	Zn(OTf) ₂	80
7	7.0	CoCl ₂ –SDS	30
8	7.0	NiCl ₂ –SDS	25
9	7.0	Cu(OTf) ₂ –SDS	90
10	7.0	Zn(OTf) ₂ –SDS	75
11	4.0	_	40
12	4.0	SDS	60
13	4.0	Zn(OTf) ₂	90
14	4.0	Zn(OTf)2–SDS	90
15	4.0	Cu(OTf) ₂	97
16	4.0	Cu(OTf) ₂ –SDS	99

^a Conversion determined by ¹H NMR spectroscopy; the remaining material was unreacted **1a**.

Poor levels of conversion were obtained when cobalt(II) chloride (CoCl₂) and nickel(II) chloride (NiCl₂) (both 1 mol%) were employed as catalysts (Table 1, entries 4, 5, 7 and 8). On the other hand, copper(II) triflate [Cu(OTf)₂] and zinc(II) triflate [Zn(OTf)₂] proved to be better catalysts and enhanced the reactivity of the aza-Diels–Alder reaction, especially when combined with sodium dodecyl sulfate (Table 1, entries 3, 6, 9 and 10).

To further explore the utility of these catalytic systems the reaction between **1a** and diene **2** was also run under acidic conditions (pH 4.0). The optimum reaction conditions were achieved when the copper(II) triflate–sodium dodec-

yl sulfate system (1 mol%) was employed. A quantitative yield of 2,3-dihydro-4-pyridone **3a** was obtained in 10 minutes (Table 1, entry 16).

The experimental procedure was extremely simple and straightforward: copper(II) triflate, sodium dodecyl sulfate, *N*-benzylideneaniline (**1a**) and diene **2** were added to the aqueous medium while the pH was kept constant. After completion of the reaction, pyridone **3a** was extracted with ethyl acetate and purified by column chromatography.

The role of the counter ion in the copper(II) triflate-sodium dodecyl sulfate catalytic system plays a crucial part in the outcome of the reaction. In fact, when copper(II) chloride (CuCl₂) or copper(II) nitrate [Cu(NO₃)₂] were employed as catalysts the reaction between **1a** and **2** did not go to completion, and together with product **3a**, enone **4a** was also detected (Figure 1). The formation of adduct **4a** suggested a Mannich-type addition mechanism instead of a concerted [4+2] cycloaddition pathway.



Figure 1 Intermediates suggesting a Mannich-type addition mechanism

As we were interested in developing a simple and sustainable procedure to access the 1,2-diphenyl-2,3-dihydro-4pyridone moiety, we next investigated if the aqueous medium and the catalytic system employed could be recycled and reused. A test reaction between *N*-benzylideneaniline (1a) and diene 2 was performed, and following completion, the aqueous solution containing the catalyst was recovered and reused twice more to promote the same aza-Diels–Alder reaction with no loss of activity being observed. Recycling of the catalyst can be repeated with similar results being obtained with complete recovery of the aqueous layer. Such results are important, making our protocol more convenient from an environmental point of view with respect to other processes showing similar chemical efficiency.

The importance of the aqueous medium was stressed by comparing the reactivity of the model reaction between 1a and diene 2 in different reaction media employing copper(II) triflate–sodium dodecyl sulfate as the catalytic system. In acetonitrile and dichloromethane good conversions were achieved, however a mixture of the desired product 3a and Mannich adduct 4a was formed. Under solvent-free conditions, slightly inferior results were obtained. Furthermore, using the aqueous medium makes recovery and reuse of the catalytic system more straightforward.

Finally, the optimized conditions (Table 1, entry 16) were employed for the preparation of a range of 1,2-diphenyl-2,3-dihydro-4-pyridones **3a–i** starting from *N*-benzylideneanilines **1a–i** and diene **2**, as reported in Table 2.

 Table 2
 Copper(II) Triflate–Sodium Dodecyl Sulfate Catalyzed

 Preparation of Pyridones 3a–i in Aqueous Medium (pH 4.0) at 30 °C

Entry	Imine	\mathbb{R}^1	R ²	Time (min)	Product	Yield (%) ^a
1	1a	Н	Н	10	3a	95
2	1b	Н	4-MeO	60	3b	88
3	1c	4-MeO	Н	60	3c	85
4	1d	4-MeO	4-MeO	60	3d	94 ^b
5	1e	Н	4-Br	30	3e	85
6	1f	4-Br	Н	120	3f	84
7	1g	Н	4-O ₂ N	60	3g	95°
8	1h	Н	2-НО	60	3h	95°
9	1i	4-0 ₂ N	Н	180	3i ^d	89°

^a Yield of isolated product.

^b Three equivalents of diene **2** were used.

^c Two equivalents of diene 2 were used.

^d Obtained after acidic treatment of adduct 4i.

The copper(II) triflate-sodium dodecyl sulfate protocol used to synthesize the pyridone **3a** worked well for derivatives **3b-h**, which were obtained in excellent 84–95% yields (Table 2, entries 2–8). In the case of *N*-benzylideneanilines, **1d**, **1g**, **1h** and **1i**, greater than stoichiometric amounts (2–3 equivalents) of diene **2** were necessary to allow the aza-Diels-Alder reaction to go to completion (Table 2, entries 4, 7, 8 and 9). The reaction between imine **1i** and diene **2** yielded the Mannich adduct **4i** (Figure 1) instead of the expected product **3i** (Table 2, entry 9), probably due to the presence of the electron-withdrawing nitro group on the aniline fragment. Nevertheless, the desired 2,3-dihydro-4-pyridone **3i** was obtained through acidic treatment of adduct **4i** [THF–1 M HCl (1:1), 1 M, 30 °C, 14 h, see experimental section].

In conclusion, the highly efficient synthesis of 1,2-diphenyl-2,3-dihydro-4-pyridones via the aza-Diels–Alder reaction between a range of *N*-benzylideneanilines **1** and Danishefsky's diene (**2**) using copper(II) triflate–sodium dodecyl sulfate as the catalytic system in acidic water (pH 4.0) has been described. The aqueous solution containing the catalyst could be recovered and reused without any loss in efficiency. Hence, the reported procedure can be considered a chemically and environmentally efficient strategy for accessing the 2,3-dihydro-4-pyridone moiety.

All chemicals were purchased from commercial suppliers and were used without any further purification. *N*-Benzylideneaniline (1a) is commercially available whereas substrates 1b-h were prepared by mixing the corresponding aldehydes and anilines for 1–3 hours at 60 °C. Imine 1i was synthesized by heating a mixture of benzalde-

hyde and 4-nitroaniline at 120 °C for 12 hours. Pyridones 3a-g are known compounds, however **3f** is not fully described in the literature. Mannich adduct 4i and pyridones 3h and 3i are new compounds. Adduct 4a was not characterized as it was only detected in the reaction forming product **3a**. Column chromatography was performed using Merck Kieselgel 60 silica gel (230-400 mesh). IR spectra were recorded on a Perkin-Elmer RXI FT-IR spectrophotometer using CHCl₃ as the solvent. ¹H (400 MHz) and ¹³C (100.6 MHz) NMR spectra were recorded on a Bruker DRX 400 Avance spectrometer. Samples were dissolved in the appropriate deuterated solvent with the residual solvent peak as the internal standard, or TMS in the case of CDCl₃. Chemical shifts are reported in ppm and coupling constants in Hz. GC-MS (EI) analyses were carried out using an Agilent HP6890N mass-selective detector equipped with an electron impact ionizer at 70 eV. Elemental analyses were recorded using a Fisons EA1008 CHNS analyzer.

1,2-Diphenyl-2,3-dihydropyridin-4(1*H*)-ones 3a-h; General Procedure

To a screw-capped vial equipped with a magnetic stir bar, H_2O (2 mL), $Cu(OTf)_2$ (1 mol%), SDS (1 mol%), *N*-benzylideneaniline **1a**–**h** (1.0 × 10⁻³ mol) and Danishefsky's diene (**2**) (1.0–3.0 × 10⁻³ mol) were added consecutively at 30 °C. The mixture was maintained at pH 4.0 by addition of HCl (1 M). After completion of the reaction, the mixture was extracted with EtOAc (2 × 3 mL), and the combined organic phase dried over Na₂SO₄ and evaporated. The crude residue was purified by column chromatography (hexane–EtOAc, 8:2) to yield pure pyridone **3a–h**. The reaction between imine **1i** and diene **2** performed under these conditions gave the corresponding Mannich adduct **4i** (0.307 g, 0.94 × 10⁻³ mol) in 94% yield as a yellow oil.

1-(4-Bromophenyl)-2-phenyl-2,3-dihydropyridin-4(1*H*)-one (3f)

Yield: 0.275 g, 0.84×10^{-3} mol (84%); colorless oil.

IR (CHCl₃): 1648, 1578, 1493, 1322 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 2.78 (dd, *J* = 2.5, 16.4 Hz, 1 H), 3.27 (dd, *J* = 7.1, 16.4 Hz, 1 H), 5.23 (d, *J* = 4.2 Hz, 1 H), 5.29 (d, *J* = 7.8 Hz, 1 H), 6.88 (d, *J* = 8.4 Hz, 2 H), 7.22–7.38 (m, 7 H), 7.61 (d, *J* = 7.9 Hz, 1 H).

¹³C NMR (100.6 MHz, CDCl₃): δ = 43.2, 61.3, 103.2, 116.9, 119.8 (2 C), 125.8 (2 C), 127.7, 128.8 (2 C), 132.2 (2 C), 137.2, 143.4, 147.4, 189.8.

GC–MS: *m/z* (%) = 329 (100) [⁸¹Br, M]⁺, 328 (26), 327 (100) [⁷⁹Br, M]⁺, 252 (72), 250 (73), 225 (97), 224 (20), 223 (99), 197 (22), 195 (22), 184 (26), 182 (26), 157 (32), 155 (31), 116 (89), 103 (21), 89 (23), 76 (21).

Anal. Calcd for $\rm C_{17}H_{14}BrNO:$ C, 62.21; H, 4.30; N, 4.27. Found: C, 62.29; H, 4.34; N, 4.12.

2-(2-Hydroxyphenyl)-1-phenyl-2,3-dihydropyridin-4(1*H*)-one (3h)

Yield: 0.252 g, 0.95×10^{-3} mol (95%); colorless oil.

IR (CHCl₃): 2254, 1643, 1771, 908 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 2.78 (d, *J* = 16.5 Hz, 1 H), 3.35 (dd, *J* = 7.4, 16.7 Hz, 1 H), 5.34 (d, *J* = 4.2 Hz, 1 H), 5.56 (d, *J* = 4.3 Hz, 1 H), 6.96–7.49 (m, 10 H), 7.56 (d, *J* = 7.7 Hz, 1 H).

¹³C NMR (100.6 MHz, CDCl₃): δ = 43.0, 54.7, 101.4, 117.6, 118.5 (2 C), 119.9, 126.6 (2 C), 127.5, 129.1 (2 C), 130.4, 148.4, 149.2, 158.3, 189.7.

Anal. Calcd for C₁₇H₁₅NO₂: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.88; H, 5.75; N, 5.31.

(1*E*)-1-Methoxy-5-[(4-nitrophenyl)amino]-5-phenypent-1-en-3one (4i) $V(x)=10, 0, 207, x, 0, 04, y, 10^{-3}, y, 1, (0,40)$

Yield: $(0.307 \text{ g}, 0.94 \times 10^{-3} \text{ mol } (94\%); \text{ yellow oil.}$ IR (CHCl₃): 1600, 1326, 1113, 910 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 2.65 (dd, *J* = 1.6, 16.5 Hz, 1 H), 3.51 (dd, *J* = 7.6, 16.8 Hz, 1 H), 3.66 (s, 3 H), 4.77–5.03 (m, 1 H), 5.50 (d, *J* = 18.3 Hz, 1 H), 5.80 (d, *J* = 4.1 Hz, 1 H), 6.48 (d, *J* = 16.5 Hz, 2 H), 7.19–7.39 (m, 5 H), 7.51 (d, *J* = 17.8 Hz, 1 H), 8.09 (d, *J* = 15.9 Hz, 2 H).

 ^{13}C NMR (100.6 MHz, CDCl₃): δ = 49.6, 53.4, 57.7, 103.3, 122.0 (2 C), 126.2 (2 C), 127.1 (2 C), 127.4, 129.8 (2 C), 138.2, 143.5, 152.3, 159.9, 199.4.

Anal. Calcd for $C_{18}H_{18}N_2O_4$: C, 66.25; H, 5.56; N, 8.58. Found: C, 66.32; H, 5.53; N, 8.54.

1-(4-Nitrophenyl)-2-phenyl-2,3-dihydropyridin-4(1*H***)-one (3i) To a screw-capped vial equipped with a magnetic stir bar were added a solution of 4i** (163.17 mg, 5.0×10^{-4} mol) in THF (1 mL) followed by HCl (1 M, 1 mL). The resulting mixture was stirred at 30 °C for 14 h and then extracted with EtOAc (2 × 3 mL). The combined organic phase was dried over Na₂SO₄ and the solvent evaporated to give pyridone **3i**.

Yield: 0.279 g, 0.95×10^{-3} mol (95%); colorless oil.

IR (CHCl₃): 1735, 1650, 1493, 1214 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 2.78 (dd, *J* = 1.8, 16.4 Hz, 1 H), 3.36 (dd, *J* = 7.6, 16.5 Hz, 1 H), 5.39 (d, *J* = 4.3 Hz, 1 H), 5.46 (d, *J* = 7.7 Hz, 1 H), 7.09 (d, *J* = 7.7 Hz, 2 H), 7.22–7.37 (m, 5 H), 7.76 (d, *J* = 8.4 Hz, 1 H), 8.18 (d, *J* = 7.9 Hz, 2 H).

¹³C NMR (100.6 MHz, CDCl₃): δ = 43.4, 62.3, 101.5, 105.6 (2 C), 118.2 (2 C), 126.2 (2 C), 127.8, 128.7 (2 C), 143.0 (2 C), 152.8, 158.4, 189.8.

Anal. Calcd for $C_{17}H_{14}N_2O_3$: C, 69.38; H, 4.79; N, 9.52. Found: C, 69.34; H, 4.83; N, 9.52.

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