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Reaction of Aldehydes and Pyrazolones in the Presence of Sodium Dodecyl Sulfate in Aqueous Media

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Abstract: The environmentally friendly condensation 3-methyl-1-phenyl-5-pyrazolone or 3-methyl-1H-5-pyrazolone with aromatic and aliphatic aldehydes was performed in water at refluxing temperature for 1 h using sodium dodecyl sulfate (SDS) as the surfactant catalyst (5 mol%), giving 4,4'-alkylmethylene-bis(3-methyl-5-pyrazolones) in 78.3%~92.1% yields.

Keywords: 4,4'-Alkylmethylene-bis(3-methyl-5-pyrazolones), aqueous media, pyrazolones, sodium dodecyl sulfate

INTRODUCTION

Most chemical reactions of organic substances conducted in the laboratory as well as in industry need organic solvents as reaction media. In 1980, Breslow discovered that the Diels–Alder reaction performed in water can be greatly accelerated.^[1] Soon it was discovered that other organic reactions (such as Claisen rearrangement,^[2] aldol condensation,^[3] Diels–Alder reaction,^[4] and Michael reaction^[5] exhibited rate enhancements in water. To date, many more organic transformations have been carried out in water.^[6]

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Address correspondence to Shu-Xiang Wang, College of Chemistry and Environmental Science, Hebei University, Key Laboratory of Analytical Science and Technology, Hezuo Road No. 88, Baoding 071002, China. Fax: +86-312-5079628; E-mail: orgsyn@mail.hbu.edu.cn Other reasons that make unique among solvents are that it is cheap, not inflammable, and more important, it is not toxic. Choice of solvent is one of the problems in performing eco-efficient processes.^[7]

Although today's environmental consciousness imposes the use of water as a solvent on both industrial and academic chemists, organic solvents are still used instead of water because most organic substances are insoluble in water. Sodium dodecyl sulfate (SDS) is a surfactant, and the surfactant used in water can make organic materials soluble, and it as stable in water, so it can solve the drawback of the reactions in water. SDS has been used in a number of organic reactions as a good catalyst. SDS used as a surfactant catalyst is a new field in the organic reactions.^[8] However, the use of SDS as a catalyst in aqueous media for the synthesis of 4,4'-alkylmethylenebis(3-methyl-5-pyrazolones) has not been reported. In this manuscript, we report a general and highly efficient route for the synthesis of those compounds using an inexpensive and commercially available SDS as catalyst. This is an efficient synthesis in aqueous media, not only preserving the simplicity but also consistently giving the corresponding products in good yields (Scheme 1).

RESULTS AND DISCUSSION

The results are summarized in Table 1, which shows that the reaction using SDS as a catalyst in aqueous media gives the corresponding products in good yields (78.3-92.1%), although it involves the elimination of a molecule of water. Similar unusual solvent effects have been previously found in other reactions.^[9]

To examine the generality of this process, several examples illustrating this method for the synthesis of those compounds were studied. As shown in Table 1, the effect of electron and the nature of substituents on the aromatic ring did not show strongly obvious effects in terms of yields under this reaction condition. Benzaldehyde and other aromatic aldehydes



Scheme 1.

Aldehydes and Pyrazolones

	R ₁	R_2	Time (h)	Yield ^a (%)	Mp (°C)	
Entry					Found	Lit. ^[10]
a	C ₆ H ₅	C_6H_5	1	86.8	171-172	174
b	$2-ClC_6H_4$	C_6H_5	1	88.7	236-237	
c	$3-ClC_6H_4$	C_6H_5	1	91.2	153-154	
d	$4-ClC_6H_4$	C_6H_5	1	91.5	207 - 209	210
	$4-ClC_6H_4$	C_6H_5	2	91.6		
	$4-ClC_6H_4$	C_6H_5	3	91.9		
	$4-ClC_6H_4$	C_6H_5	4	92.1		
e	2, 4-Cl ₂ C ₆ H ₄	C_6H_5	1	90.2	228 - 230	231
f	$2-NO_2C_6H_4$	C_6H_5	1	88.7	224-225	
g	$3-NO_2C_6H_4$	C_6H_5	1	88.4	149 - 150	152
h	$4-NO_2C_6H_4$	C_6H_5	1	90.6	230-232	231
i	$4-HOC_6H_4$	C_6H_5	1	88.3	152-153	152
j	$4-CH_3C_6H_4$	C_6H_5	1	90.8	203 - 204	204
k	3-OCH ₃ -4-OHC ₆ H ₃	C_6H_5	1	92.1	200-201	199
1	Н	C_6H_5	1	90.0	227 - 229	
m	isobutyraldehyde	C_6H_5	1	78.3	213-214	
n	C_6H_5	Н	1	87.0	230-232	
0	$4-ClC_6H_4$	Н	1	83.7	224-226	
р	$4-HOC_6H_4$	Н	1	80.7	262-264	
q	$3-NO_2C_6H_4$	Н	1	88.8	271-272	
r	$4-NO_2C_6H_4$	Н	1	91.2	300-302	

Table 1. Synthesis of 4,4'-arylidene-bis(3-methyl-pyrazolones) in water

^aIsolated yield.

containing electron-withdrawing groups (such as a nitro group, halide) or electron-donating groups (such as a hydroxy group) were employed and reacted well with 3-methyl-1-phenyl-5-pyrazolone to give 4,4'-alkylmethylenebis-(3-methyl-1-phenyl-5-pyrazolones) in good to excellent yields. At the same time, the aliphatic aldehydes also give the corresponding products in good yields (see entries **l** and **m**). When changing 3-methyl-1-phenyl-5-pyrazolone into 3-methyl-1H-5-pyrazolone, a similar result was given; the reaction gave the corresponding compounds in good yields (see entries $\mathbf{n}-\mathbf{r}$).

The catalyst plays a crucial role in the reaction. For example, **1d** reacted with **2** without any catalyst at refluxing temperature in water for 1 h to give the product **3d** in modest yield (57.4%). While using SDS (5 mol%) as catalyst, the reaction give a white product in 91.5% yield at the same condition. By changing the mount of the catalyst from 2.5 mol% to 5 mol%, 7.5 mol%, and 10 mol%, the reaction results in **3d** at 87.7%, 91.5%, 91.9%, and 92.4%, respectively. Higher amounts of the catalyst did not improve the

yields to a greater extent. And, under the identical condition, the yield of the reaction was not affected in the presence of 5 mol% SDS after different time intervals (1 h, 2 h, 3 h, and 4 h). Thus, 5 mol% SDS was chosen as a quantitative catalyst for these reactions and 1 h was chosen as the reaction time. The catalyst could be reused 6 times for the synthesis of **3d** without significant loss of activity (as show in Table 2). SDS is an emulsifying agent, which catalyzes this reaction and forms the stable colloidal particles in the presence of the substrates in water and this colloid formation plays an important role in acceleration of the reactions. In addition, it must be pointed out that all of these reactions were carried out in water and those products were characterized by mp, IR, ¹H NMR, and elemental analyses.

In summary, a procedure for the preparation of 4,4'-alkylmethylene-bis-(3-methyl-5-pyrazolones) in aqueous media using SDS as the surfactant catalyst (5 mol%) has been developed. It is noteworthy that the experimental procedure is very simple, and strict anhydrous conditions are not required. Water solution is a clean and environmentally desirable system. No harmful organic solvents are used. This report has proposed and demonstrated a new useful and attractive process for the synthesis of these compounds.

EXPERIMENTAL

Liquid aldehydes were purified by distillation prior to use. Melting points are uncorrected. IR spectra were recorded on a Bio-Rad FTS-40 spectrometer (KBr). Elemental analyses were measured on a Heraeus (CHNO, Rapid) analyzer. ¹H NMR spectra were measured on a Bruker Avance (400 MHz) spectrometer using TMS as internal standard.

General Procedure

Pyrazolone (2 mmol), aldehyde (1.0 mmol), and SDS (0.05 mmol) in water (20 mL) were added to a flask and were stirred at room temperature for 0.5 h. Then the mixture was stirred at refluxing for 1 h. After completion of the reactions, the mixture was cooled to room temperature, the solid was filtered off and washed with H_2O , and the crude products were obtained. The crude products were purified by recrystallization from ethanol (95%).

 Times
 1
 2
 3
 4
 5
 6

 Yield/%
 91.3
 90.7
 90.2
 89.7
 88.8
 88.2

Table 2. Reuse of the catalyst for syntheses of 3d

Aldehydes and Pyrazolones

3b. Anal. calcd. for C₂₇H₂₃ClN₄O₂:C, 68.71; H, 4.91; N, 11.87. Found: C, 68.55; H, 4.48; 12.05. IR (KBr): ν_{max} : 3450, 3060, 2925, 1620, 1560, 1505, 1441, 1367, 1299, 844, 757 cm⁻¹. ¹H NMR (DMSO): δ : 2.24 (s, 6H, CH₃), 5.03 (s, IH, CH), 7.23–7.25 (m, 2H, ArH), 7.40–7.42 (m, 8H, ArH), 7.73–7.75 (m, 4H, ArH).

3c. Anal. calcd. for $C_{27}H_{23}CIN_4O_2$: C, 68.71; H, 4.91; N, 11.87. Found: C, 68.46; H, 5.05; 11.62. IR (KBr): ν_{max} : 3426, 3100, 2987, 1600, 1472, 1429, 1366, 1296, 1100, 1074, 870, 745 cm⁻¹. ¹H NMR (DMSO): δ : 2.33 (s, 6H, CH₃), 4.99 (s, 1H, CH), 7.24–7.31 (m, 5H, ArH), 7.33–7.35 (m, 1H, ArH), 7.43–7.47 (m, 4H, ArH), 7.70–7.72 (m, 4H, ArH).

3f. Anal. calcd. for $C_{27}H_{23}N_5O_4$: C, 67.21; H, 4.80; N, 14.51. Found: C, 67.15; H, 4.91; 14.36. IR (KBr): ν_{max} : 3441, 3048, 2951, 1642, 1559, 1439, 1352, 1294, 1246, 880, 828, 736 cm⁻¹. ¹H NMR (DMSO): δ : 2.25 (s, 6H, CH₃), 5.44 (s, 1H, CH), 7.22–7.29 (m, 2H, ArH), 7.42–7.49 (m, 5H, ArH), 7.63–7.73 (m, 7H, ArH).

31. Anal. calcd. for $C_{21}H_{20}N_4O_2$: C, 69.98; H, 5.59; N, 15.55. Found C, 69.73; H, 5.47; 15.38. IR (KBr): ν_{max} : 3440, 3059, 2884, 2781, 1577, 1497, 1406, 1363, 1312, 1179, 904, 794, 751, 686 cm⁻¹. ¹H NMR (DMSO): δ : 2.23 (s, 6H, CH₃), 3.24 (s, 2H, CH₂), 7.23–7.25 (m, 2H, ArH), 7.42–7.46 (m, 4H, ArH), 7.70–7.72 (m, 4H, ArH).

3m. Anal. calcd. for $C_{24}H_{26}N_4O_2$: C, 71.62; H, 6.51; N, 13.92. Found: C, 71.54; H, 6.62; 13.85. IR (KBr): ν_{max} : 3428, 3061, 2959, 2733, 1585, 1499, 1420, 1291, 1182, 1122, 1027, 901, 791, 750, 638 cm⁻¹. ¹H NMR (DMSO): δ : 0.84 [S, 6H, CH(CH₃)₂], 2.21 (s, 6H, CH₃), 2.50–2.64 [m, 1H, CH(CH₃)₂], 2.99–3.01 [d, 1H, CHCH(CH₃)₂], 7.22–7.25 (m, 2H, ArH), 7.42–7.46 (m, 4H, ArH), 7.70–7.72 (m, 4H, ArH).

3n. Anal. calcd. for $C_{15}H_{16}N_4O_2$: C, 63.37; H, 5.67; N, 19.71. Found: C, 63.54; H, 5.42; N, 20.05. IR (KBr): ν_{max} : 3415, 1606, 1530, 1491, 1388, 1143, 823, 783, 723 cm⁻¹. ¹H NMR (DMSO): δ : 2.08 (s, 6H, CH₃), 4.82 (m, 1H, CH), 7.13–7.14 (d, 3H, ArH), 7.19–7.23 (m, 2H, ArH).

30. Anal. calcd. for $C_{15}H_{15}ClN_4O_2$: C, 56.52; H, 4.74; N, 17.58. Found: C, 56.41; H, 4.42; N, 17.36 IR (KBr): ν_{max} : 3437, 1614, 1488, 1388, 1094, 757 cm⁻¹. ¹H NMR (DMSO): δ : 2.08 (s, 6H, CH₃), 4.82 (m, 1H, CH), 7.12 (s, 2H, ArH), 7.27 (m, 2H, ArH).

3p. Anal. calcd. for $C_{15}H_{16}N_4O_3$: C, 59.99; H, 5.37; N, 18.66. Found: C, 59.80; H, 5.42; N, 18.36. IR (KBr): ν_{max} : 3266, 1561, 1514, 1466, 1400, 1174, 872, 786, 731 cm⁻¹. ¹H NMR (DMSO): δ : 2.06 (s, 6H, CH₃), 4.71 (m, 1H, CH), 6.58–6.60 (d, 2H, ArH), 6.90–6.92 (d, 2H, ArH).

3q. Anal. calcd. for $C_{15}H_{15}N_5O_4$: C, 54.71; H, 4.59; N, 21.27. Found: C, 54.50; H, 4.45; N, 20.98. IR (KBr): ν_{max} : 3419, 2961, 1599, 1447, 1390, 1182, 837, 795, 764 cm⁻¹. ¹H NMR (DMSO): δ : 2.11 (s, 6H, CH₃), 4.99 (ms, 1H, CH), 7.54–7.57 (d, 2H, ArH), 7.96 (s, 1H, ArH), 8.03–8.04 (s, 1H, ArH).

3r. Anal. calcd. for C₁₅H₁₅N₅O₄: C, 54.71; H, 4.59; N, 21.27. Found: C, 54.52; H, 4.43; N, 21.05. IR (KBr): ν_{max} : 3419, 2961, 1603, 1510, 1442, 1346,

1178, 880, 800, 772 cm^{-1} . ¹H NMR (DMSO): δ : 2.10 (s, 6H, CH₃), 4.98 (s, 1H, CH), 7.36–7.39 (d, 2H, ArH), 8.11–8.13 (d, 2H, ArH).

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