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Synthesis and Fluorescence Properties of a, a'-Bis(substitutedbenzylidene)cycloalkanones Catalyzed by 1-Methyl-3(2-(sulfooxy)ethyl)-1Himidazol-3-ium Chloride

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> SYNTHESIS AND FLUORESCENCE PROPERTIES OF α, α' -BIS(SUBSTITUTED-BENZYLIDENE)-CYCLOALKANONES CATALYZED BY 1-METHYL-3(2-(SULFOOXY)ETHYL)-1*H*-IMIDAZOL-3-IUM CHLORIDE

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 α, α' -Bis(substituted-benzylidene) cycloalkanones were synthesized via a solvent-free crossaldol condensation of aromatic aldehydes with cycloalkanones in the presence of a catalytic amount 1-methyl-3(2-(sulfooxy)ethyl)-1H-imidazol-3-ium chloride at room temperature with excellent yields. The screening for optical properties indicated that the size of cycloalkanone has an influence on the fluorescence emission of products. Products coming from cyclohexanone have stronger fluorescence emission than those from cyclopentanone.

Keywords: α, α' -Bis(substituted-benzylidene)cycloalkanones; cross-aldol condensation; fluorescence; synthesis

INTRODUCTION

Cross-aldol condensation of aromatic aldehydes with cyclic ketones is an important method for the preparation of α, α' -bis(substituted-benzylidene)cycloalkanones. The resulting benzylidene derivatives, which have many conjugated unsaturated linkages, are versatile building blocks for many compounds such as pharmaceuticals, agrochemicals and perfumes, new organic materials for nonlinear optical application,^[1] cytotoxic analogs,^[2] and the units of liquid-crystalline polymers.^[3] Moreover, they can be used to synthesize some multifunctional group compounds with special structures via Diels–Alder reaction, Michael addition,^[4] and so on. Therefore, it is important to research its synthetic process.

Cross-aldol condensation is classically catalyzed by a strong acid or base. However, these processes suffer from reverse and side reactions, resulting in poor

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Scheme 1. Synthesis of α, α' -bis(substituted-benzylidene) cycloalkanones.

yields of the products.^[5] Different complexes of metal(II) ions have also been used as catalysts, but the yields were less than 38%.^[6] In other cases, Cp₂TiPh₂,^[7] BOMPTO [bis(*p*-ehtoxyphenyl)telluroxide],^[8] RuCl₃,^[9] SmI₃,^[10] Cp₂ZrH₂,^[11] TiCl₃(SO₃CF₃),^[12] KF·Al₂O₃,^[13] FeCl₃,^[14] BF₃·OEt₂,^[15] InCl₃,^[16] TMSCl/NaI,^[17] Yb(OTf)₃,^[18] I₂^[19], TCT^[20], NaOAc/HOAc,^[21] and NKC-9 (polymer-supported sulfonic acid)^[22] have also been used to promote the reaction. However, these methods have some drawbacks such as use of costly catalysts and toxic reagents and special catalyst preparation.

Ionic liquids have generated a great amount of interest in organic chemistry as reaction solvents and catalysts^[23–28] in recent years and are emerging as "green reaction media." Product isolation is very easy in ionic liquids, and in many cases rate accelerations or selectivity improvements are also observed.

In this article, we report the catalytic potential of 1-methyl-3(2-(sulfooxy)ethyl)-1H-imidazol-3-ium chloride (I), which was prepared simply in our laboratory from the condensations of aromatic aldehydes and cyclicketones as both green solvent and catalyst (Scheme 1).

RESULTS AND DISCUSSION

Initially, six Brønsted or Lewis acid were tested in the reaction of 4-methoxylbenzaldehyde (4.2 mmol) and cyclohexanone (2.0 mmol) at room temperature (Scheme 2, Table 1). No product was detected in the control reaction (Table 1, entry 1), and weak acids dodecyl sulfate sodium (SDS) and HOAc (Table 1, entries 5 and 6) did not catalyze this reaction. Silica sulfuric acid, TsOH, HCl, and I (Table 1, entries 2–4 and 7) promoted the reaction, and I was the most potent catalyst of this reaction with 96% yield (Table 1, entry 7). Increasing the catalytic load of I from 0.06 mol% to 0.10 mol% improved the yield from 82% to 96%, which showed that the catalyst concentration plays a major role in the reaction. However, the yield decreased unexpectedly when the amount of catalyst was more than 0.10 mol%. A possible explanation for the decrease of yield is that the reaction could drive the



Scheme 2. Six catalysts were tested in the reaction of 4-methoxylbenzaldehyde and cyclohexanone at room temperature.

Entry	Catalyst	X (mol%)	Time (h)	Yield ^a (%)
1	_		24	Nr ^c
2	Silica sulfuric acid	0.10	12	60
3	TsOH	0.10	10	78
4	HCl	0.10	5	73
5	SDS^b	0.10	24	Nr^{c}
6	HOAc	0.10	24	Nr^{c}
7	Ι	0.10	1	96
8	Ι	0.06	1	82
9	Ι	0.08	1	85
10	Ι	0.12	1	89

Table 1. Control reaction with added amounts of catalyst

^aYield of isolated product.

^bSodium dodecyl sulfate (SDS).

^cNo reaction.

equilibrium toward reactants when an excess amount (0.12 mol%) of I was added, and thus 0.10 mol% of I is suitable choice for optimum yield of 2,6-bis(4-methoxybenzylidene)cyclohexanone (Table 1, entries 7–10).

Table 2. Cross-aldol reaction of aromatic aldehydes and cyclicketones^a

	Ar	n	Time (h)	Product		Mp (°C)	
Entry					Yield ^b (%)	Found	Reported
1	4-OCH ₃ C ₆ H ₄	1	2.5	3a	92	210-211	211-212 ^[18]
2	$4-FC_6H_4$	1	2	3b	92	236-237	237-239 ^[19]
3	$3-FC_6H_4$	1	2	3c	91	88-89	
4	$4-BrC_6H_4$	1	2	3d	93	251-253	
5	$3-BrC_6H_4$	1	2	3e	91	179-181	
6	3,4-OCH ₂ OC ₆ H ₃	1	1	3f	94	257-259	
7	4-CNC ₆ H ₄	1	3	3g	88	>300	
8	3-ClC ₆ H ₄	1	2	3h	90	228-229	228-229 ^[18]
9	3-NO ₂ C ₆ H ₄	1	3	3i	86	226-227	
10	C ₆ H ₅	2	2	3j	90	115-116	117-118 ^[18]
11	4-OCH ₃ C ₆ H ₄	2	1	3k	96	156-157	161–163 ^[18]
12	$4-FC_6H_4$	2	1	31	94	157-159	156–158 ^[17]
13	$3-FC_6H_4$	2	2	3m	91	87-88	
14	$3-BrC_6H_4$	2	2	3n	91	118-119	119-121 ^[22]
15	$4-BrC_6H_4$	2	1	30	93	164-165	165–168 ^[21]
16	$2-BrC_6H_4$	2	2	3р	88	111-112	
17	3,4-OCH ₂ OC ₆ H ₃	2	1	3q	95	182-183	
18	4-CNC ₆ H ₄	2	3	3r	89	229-230	
19	4-ClC ₆ H ₄	2	1	3s	92	146-147	147–148 ^[9]
20	3-NO ₂ C ₆ H ₄	2	3	3t	89	198-200	200-202 ^[19]
21	3,4-OCH ₃ C ₆ H ₃	2	1	3u	94	143-144	
22	3,4,5-OCH ₃ C ₆ H ₂	2	1	3v	96	205-206	

^{*a*}Reaction conditions: aromatic aldehyde (4.2 mmol) and cyclic ketone (2.0 mmol) were stirred at room temperature in the presence of I (0.10 mol%) for the given time.

^bYield of isolated product.



Figure 1. Fluorescent emission spectrum of α, α' -bis(substituted-benzylidene)cycloalkanones (1–22: 3a, 3c, 3b, 3d, 3h, 3g, 3f, 3e, 3u, 3l, 3s, 3k, 3r, 3i, 3o, 3j, 3m, 3n, 3v, 3p, 3q, 3t).

Compound	$\begin{array}{c} E_{max}(abs) \\ (M^{-1}cm^{-1}) \end{array}$	$\lambda_{max(ex)}$ (nm)	$\lambda_{max(em)}$ (nm)	RFI ^a	Stokes (nm)	$\Phi_{ m F}{}^b$
9,10-Diphe nylanthracene	2.448	260	408	2793	148	0.660
3a	2.462	256	308	588	52	0.140
3b	2.377	254	308	602	54	0.138
3c	2.468	259	309	589	50	0.140
3d	2.452	257	308	611	51	0.145
3e	2.472	258	310	688	52	0.164
3f	2.479	261	311	680	50	0.163
3g	2.460	258	308	678	50	0.161
3h	2.528	258	309	612	51	0.149
3i	2.441	253	307	1688	54	0.398
3j	2.333	253	307	1697	54	0.382
3k	2.379	253	307	1669	54	0.383
31	2.484	253	308	1655	55	0.397
3m	2.438	252	307	1703	55	0.401
3n	2.413	252	307	1704	55	0.397
30	2.466	254	308	1694	54	0.403
3р	2.408	252	308	1727	56	0.401
3q	2.406	253	307	1774	54	0.412
3r	2.490	253	307	1685	54	0.405
3s	2.394	253	308	1668	55	0.385
3t	2.523	255	308	1816	53	0.442
3u	2.487	252	307	1631	55	0.392
3v	2.368	252	307	1706	55	0.390

Table 3. Luminescence of products

^aRelative fluorescence intensity.

^bRelative fluorescence quantum yield.

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Having optimized the cross-aldol condensation in the presence of I, we decided to screen a series of aromatic aldehydes (2) and cyclopentanone/cyclohexanone (1) to evaluate the scope of this reaction. The results summarized in Table 2 show that excellent yields were achieved for most of the substrates. It appeared that the electronic nature of the substituted group in aromatic aldehyde has little influence on yields; both the electron-donating (Me, MeO) and electron-withdrawing (NO₂, Cl) groups worked well with little distinction.

The fluorescence properties of products are shown in Fig. 1 and Table 3 with better fluorescence efficiency. The following conclusions are clear: (i) All products have similar fluorescence spectra, and the electro- and steric effects of the substituted group on aromatic aldehydes have little influence on the fluorescence properties, which clearly showed that the luminescence of products come from their framework directly. (ii) The size of cycloalkanone has an effect on the fluorescence emission of products. Products coming from cyclohexanone have stronger fluorescence emission than those from cyclopentanone (Fig. 1). Interestingly, in these two series, compounds **3i** and **3t** (which both derive from 3-nitrobenzaldehyde) have the strongest fluorescence emission. The possible reason could be due to the different conformational preferences and the different levels of coplanarity of the extended π systems. (iii) Besides **3a-h**, other products exhibited stronger fluorescence in EtOH on the presence of 9,10-diphenylanthracence ($\Phi_F = 0.660$, EtOH), which showed their potential application as new fluorescent probes or luminescence materials.

EXPERIMENTAL

All reagents were purchased from commercial sources and used without further purification. Thin-layer chromatography (TLC) was performed with glass-backed plates precoated with silica gel and examined under ultraviolet (UV) light (254 nm). NMR spectra were measured in CDCl₃ with Me₄Si as the internal standards on a Bruker Advance DPX-400 instrument at room temperature. Infrared (IR) spectra were recorded on Bruker Fourier transform (FT)–IR spectrometer, and absorbances were reported in centimeters⁻¹. Fluorescence properties were reported on a F-4500 fluorescence spectrophotometer (Hitachi, Japan). The absorption spectrum was measured with a Tu-1201 UV spectrophotometer (Shimadzu). Mass spectra (MS) were determined by using a Bruker MicroTOF-QII highresolution mass spectrometer.

General Procedure for the Preparation of 1-Methyl-3(2-(sulfooxy)ethyl)-1*H*-imidazol-3-ium Chloride

A mixture of 1-methylimidazole (0.3 mol), chloroethanol (0.3 mol), and 10 mL of CHCl₃ was refluxed for 8 h, and then CHCl₃ was removed under vacuum. Extraction of the unreacted 1-methylimidazole with ether gave 1-methyl-3-(2-hydroxylethyl)imidazolium chloride. Then chlorosulfonic acid was added dropwise at 0-5 °C; when the mixture became solid, a suitable single crystal was obtained after 3 days by recrystallization with dimethylformamide (DMF). This solid inner salt reacted with chlorosulfonic acid continuously until it became a ropy liquid, 1-methyl-3(2-(sulfooxy)ethyl)-1*H*-imidazol-3-ium chloride.

General Procedure for Preparation of Compounds 3

A mixture of aromatic aldehyde (4.2 mmol), cycloalkanone (2.0 mmol), and I (0.10 mol%) was stirred at room temperature for 1-3 h (if solid aldehyde was used, 5 drops of anhydrous ethanol were added to the mixture to make it dissolve completely). Upon completion (monitored by TLC), water was added and the catalyst was removed by filtration. The product was purified by recrystallization with EtOH. The analytical data for representative compounds are shown.

Ultraviolet and Fluorescence Measurement of Compounds 3

The EtOH solutions of **3a-v** $(1.0 \times 10^{-6} \text{ mol/L})$ were measured on UV and fluorescence spectrophotometers to give their absorption and emission spectra, respectively.

Spectral Data of New Products

2,5-Bis(3-fluorobenzylidene)cyclopentanone (3c). ¹H NMR (400 MHz, CDCl₃) δ : 3.10 (s, 4H), 7.07 (t, J = 8.0 Hz, 2H), 7.22 (dd, J = 7.2 Hz, J = 10.0 Hz, 4H), 7.37–7.43 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ : 195.53, 163.84, 161.39, 137.87, 137.57, 132.48, 130.05, 126.46, 116.31, 26.15; IR (KBr, ν , cm⁻¹): 3024, 1705, 1619, 1608, 1556; MS (ESI) for C₁₉H₁₄F₂O [M+H] found (expected): 297.1080 (297.1091).

2,5-Bis(4-bromobenzylidene)cyclopentanone (3d). ¹H NMR (400 MHz, CDCl₃) δ : 3.11 (s, 4H), 7.48 (d, J = 8.0 Hz, 4H), 7.55 (s, 2H), 7.60 (d, J = 8.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ : 189.73, 137.92, 137.08, 135.53, 132.81, 131.53, 129.94, 128.93, 122.51, 28.33; IR (KBr, ν , cm⁻¹): 3069, 1865, 1688, 1625, 1605; MS (ESI) for C₁₉H₁₄Br₂O [M + H] found (expected): 416.9511 (416.9490).

2,5-Bis(3-bromobenzylidene)cyclopentanone (3e). ¹H NMR (400 MHz, CDCl₃) δ : 3.12 (s, 4H), 7.14–7.18 (m, 4H), 7.59–7.63 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ : 195.76, 138.22, 137.76, 133.14, 132.51, 132.31, 130.30, 129.32, 122.93, 26.41; IR (KBr, ν , cm⁻¹): 3055, 1854, 1649, 1605, 1588; MS (ESI) for C₁₉H₁₄Br₂O [M + H] found (expected): 416.9509 (416.9490).

2,5-Bis((benzo[*d***][1,3]dioxol-5-yl)methylene) cyclopentanone (3f).** ¹H NMR (400 MHz, CDCl₃) δ : 3.09 (s, 4H), 6.05 (s, 4H), 6.91 (d, J = 8.0 Hz, 2H), 7.13–7.17 (m, 4H), 7.53 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ : 195.20, 148.73, 148.12, 135.54, 133.59, 130.35, 126.75, 109.77, 108.79, 101.57, 26.51; IR (KBr, ν , cm⁻¹): 3056, 1706, 1660, 1600; MS (ESI) for C₂₁H₁₆O₅ [M + H] found (expected): 349.1116 (349.1076).

2,5-Bis(4-cyanobenzylidene)cyclopentanone (3g). ¹H NMR (400 MHz, CDCl₃) δ : 3.26 (s, 4H), 7.65–7.69 (m, 4H), 7.91 (d, J = 8.0 Hz, 2H), 8.27–8.29 (m, 2H), 8.49 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ : 194.71, 154.62, 150.65, 149.11, 148.02, 134.45, 130.56, 26.54; IR (KBr, ν , cm⁻¹): 3106, 2256, 1706, 1649, 1608, 1522; MS (ESI) for C₂₁H₁₄N₂O [M + H] found (expected): 311.1164 (311.1184).

2,5-Bis(3-nitrobenzylidene)cyclopentanone (3i). ¹H NMR (400 MHz, CDCl₃) δ 3.13 (s, 4H), 7.32–7.36 (m, 2H), 7.52–7.54 (m, 6H), 7.74 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ : 195.33, 148.63, 139.24, 137.15, 136.42, 131.73, 129.91, 124.51, 123.93, 26.40; IR (KBr, ν , cm⁻¹): 3069, 1728, 1640, 1606, 1524; MS (ESI) for C₁₉H₁₄N₂O₅ [M + H] found (expected): 351.0995 (351.0981).

2,6-Bis(3-fluorobenzylidene)cyclohexanone (3m). ¹H NMR (400 MHz, CDCl₃) δ : 1.78–1.85 (m, 2H), 2.88–2.94 (m, 4H), 6.97–7.10 (m, 2H), 7.13–7.27 (m, 4H), 7.35–7.50 (m, 2H), 7.74 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ : 189.91, 163.83, 161.39, 138.03, 136.97, 135.81, 129.99, 126.30, 116.83, 115.68, 28.38, 22.78; IR (KBr, ν , cm⁻¹): 3023, 1705, 1619, 1608, 1556; MS (ESI) for C₂₀H₁₆F₂O [M + H] found (expected): 311.1356 (311.1247).

2,6-Bis(2-bromobenzylidene)cyclohexanone (3p). ¹H NMR (400 MHz, CDCl₃) δ 1.77–1.80 (m, 2H), 2.76–2.79 (m, 4H), 7.20–7.24 (m, 2H), 7.34–7.36 (m, 4H), 7.66 (d, J = 7.6 Hz, 2H), 7.87 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ : 189.67, 137.44, 136.42, 136.29, 132.98, 130.55, 129.74, 126.90, 125.17, 28.32, 23.15; IR (KBr, ν , cm⁻¹): 3067, 1845, 1625, 1589, 1558; MS (ESI) for C₂₀H₁₆Br₂O [M + H] found (expected): 430.9647 (430.9646).

2,6-Bis((benzo[d][1,3]dioxol-5-yl)methylene)cyclohexanone (3q). ¹H NMR (400 MHz, CDCl₃) δ 1.81–1.84 (m, 2H); 2.92 (t, J=5.2 Hz, 4H), 6.03 (s, 4H), 6.87 (d, J=8.0 Hz, 2H), 7.01–7.04 (m, 4H), 7.73 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ : 190.06, 148.02, 147.71, 136.73, 134.65, 130.20, 125.86, 110.06, 108.44, 101.39, 28.54, 22.96; IR (KBr, ν , cm⁻¹): 3058, 1706, 1660, 1600; MS (ESI) for C₂₂H₁₈O₅ [M + H] found (expected): 363.1313 (363.1232).

2,6-Bis(4-cyanobenzylidene)cyclohexanone (3r). ¹H NMR (400 MHz, CDCl₃) δ : 1.85–1.86 (m, 2H), 2.94 (t, J = 5.2 Hz, 4H), 7.56 (d, J = 8.0 Hz, 4H), 7.72–7.78 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ : 189.01, 140.02, 138.07, 134.92, 131.90, 130.34, 130.62, 118.24, 111.81, 28.07, 22.35; IR (KBr, ν , cm⁻¹): 3104, 2256, 1706, 1649, 1608, 1522; MS (ESI) for C₂₂H₁₆N₂O [M + H] found (expected): 325.1344 (325.1341).

2,6-Bis(3,4-dimethoxybenzylidene) cyclohexanone (3u). ¹H NMR (400 MHz, CDCl₃) δ : 1.84–1.86 (m, 2H), 2.97 (t, J = 5.2 Hz, 4H), 3.94 (d, J = 4.0 Hz, Hz, 12H), 6.93 (d, J = 8.4 Hz, 2H), 7.05 (s, 2H), 7.14 (d, J = 8.4 Hz, 2H), 7.78 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ : 190.05, 149.63, 148.68, 136.83, 134.52, 129.01, 123.94, 113.74, 110.91, 55.96 (×2), 28.55, 23.06; IR (KBr, ν , cm⁻¹): 3013, 1703, 1661, 1595, 1505, 1248; MS (ESI) for C₂₄H₂₆O₅ [M+H] found (expected): 395.1912 (395.1858).

2,6-Bis(3,4,5-trimethoxybenzylidene)cyclohexanone (3v). ¹H NMR (400 MHz, CDCl₃) δ : 1.85–1.87 (m, 2H), 2.98 (t, J = 5.2 Hz, 4H), 3.89–3.92 (m, 18H), 6.73–6.75 (m, 4H), 7.75 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ : 189.98, 153.01, 138.78, 137.15, 135.40, 131.46, 107.88, 61.02, 56.73, 28.48, 23.02; IR (KBr, ν , cm⁻¹): 3025, 1708, 1665, 1585, 1505, 1345; MS (ESI) for C₂₆H₃₀O₇ [M + H] found (expected): 455.2114 (455.2070).

CONCLUSION

In conclusion, we have developed a simple and efficient cross-aldol condensation of aromatic aldehydes with cyclic ketones to form α, α' -bis(substituted-benzylidene) cycloalkanones using 1-methyl-3(2-(sulfooxy)ethyl)-1*H*-imidazol-3-ium chloride as catalyst at room temperature. Because of its benefits, the protocol may be used to synthesize a variety of multifunctional compounds. Some products have potential application as new fluorescent probes, luminescence materials, or ligands. Future effort to explore the coordination function of products is under way.

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