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Development of Highly Effective Encapsulating Surfactants for Mukaiyama Aldol Reactions in Water

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Amphiphilic calix[6]arene derivatives **1a–b** and calix[4]arene **1d–1e**, as well as aliphatic (**2a–b**) and aromatic (**2c–2d**) anionic surfactants, were studied for their encapsulating ability in stabilizing water-sensitive compounds. They were found to be efficient surfactants for Sc(OTf)₃-catalyzed Mukaiyama aldol reactions of labile enol ethers with aldehydes in water. The results indicate that a hydrophobic microenvironment was formed in the reaction system with either the amphiphilic calix[6]arene derivatives or the simple aromatic surfactants, which could encapsulate and stabilize some labile silyl enol ethers and thus promote the reactions.

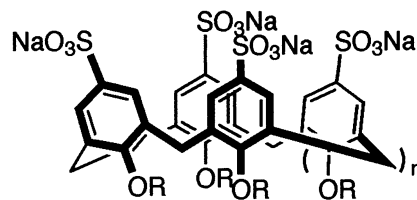
Introduction

Organic reactions in water, which avoid the use of harmful organic solvents, are now of great interest, especially in relation to today's environmental concerns.¹ Although it would be best not to use any solvent, frequently (for various reasons) a solvent is required for a reaction. In such cases, the use of some solvents such as water is desirable. The development of carbon–carbon bond-forming reactions in aqueous media is a challenging topic in organic synthesis.² Many organic reagents or intermediates are sensitive to water, which limits the scope of aqueous reactions. However, we postulated that, by using an encapsulating surfactant, these water-sensitive reagents and intermediates could be stabilized, thereby effecting subsequent transformations in water. Recently, Kobayashi and co-workers reported the notion of creating “hydrophobic pockets” using a series of benzene rings separated by flexible alkyl linkers.³ Herein, we report the development of a group of surfactants that are highly effective in encapsulating water-sensitive species and facilitating the Mukaiyama aldol reaction in water.⁴

The aldol-type reaction of silyl enol ethers with carbonyl compounds (the Mukaiyama reaction⁵) has been recognized as one of the most important carbon–carbon bond-forming reactions. Recently, great progress has been made toward the achievement of aqueous Mukaiyama aldol reactions using a series of water-tolerant Lewis acids, such as lanthanide triflates and metal salts.⁶ As Kobayashi⁷ reported, to effect the reactions in water alone, certain surfactants must be used so that a micellar system is formed. These surfactants can be anionic, such as sodium dodecyl sulfate (SDS, **2a**), or nonionic. However, despite the effectiveness of these surfactants in promoting the reaction between aldehydes and stable silyl enol ethers, very labile silyl enol ethers decompose rapidly in these systems, leading to very low yields of the desired

products. To improve the reaction yield, it is necessary to use a large excess of the very labile silyl enol ethers in these systems.⁸

Previously, Shinkai and co-workers⁹ reported the inclusion properties of some water-soluble calixarene derivatives with surfactant activities. It was found that water-soluble *p*-sulfonated calixarenes could form host–guest-type complexes with various organic guest molecules in water through hydrophobic interactions. We envisioned that the use of these calixarene derivatives as surfactants in the aqueous Mukaiyama aldol reaction would provide a hydrophobic cavity that could encapsulate and stabilize the unstable silyl enol ethers and thus prevent them from being hydrolyzed in water. Herein, we report the study of the calix[6]arenes **1b** and **1c** (bearing both sulfonates and alkyl groups), as well as aliphatic (**2a** and **2b**) and aromatic (**2c** and **2d**) anionic surfactants as potential encapsulating surfactants for Sc(OTf)₃-catalyzed-Mukaiyama reactions in water (eq 1).



$n=3$

$n=1$

1a R=*n*-C₄H₉

1d R=*n*-C₆H₁₃

1b R=*n*-C₆H₁₃

1e R=*n*-C₁₂H₂₅

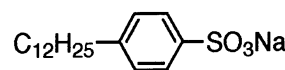
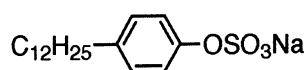
1c R= H

C₁₂H₂₅OSO₃Na

C₁₂H₂₅SO₃Na

2a

2b



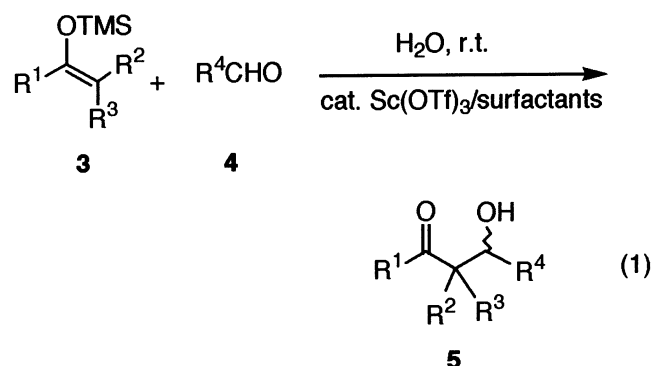
2c

2d

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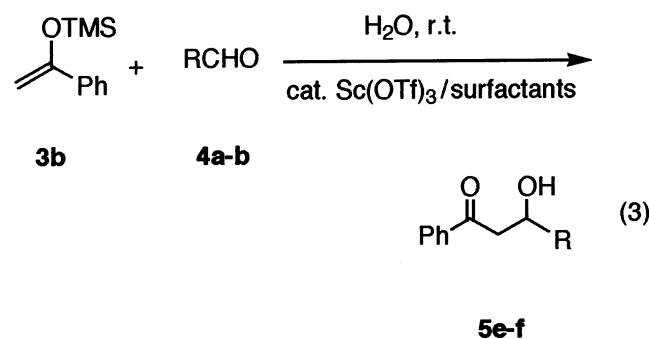
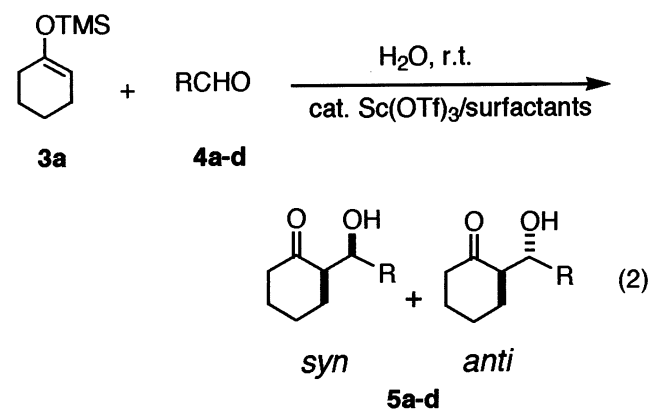
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Results and Discussions

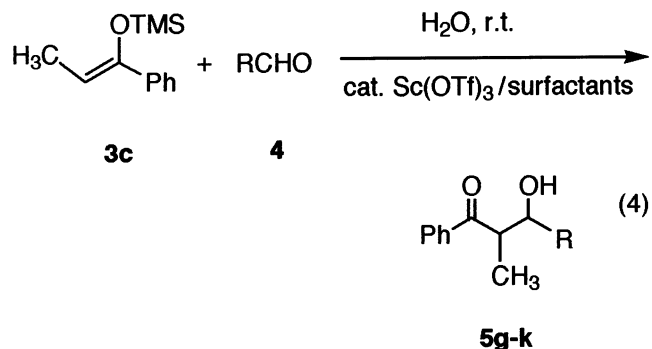
Encapsulating Effect of Calix[6]arene Derivatives. Calix[6]arene derivatives **1a–1c** and calix[4]arene derivatives **1d–1f** bearing sulfonate groups on the upper rim and various groups on the lower rim were synthesized using Shinkai's method.⁹ The aldol reactions of silyl enol ethers 1-trimethylsilyloxycyclohex-1-ene (**3a**) and 1-phenyl-1-trimethylsiloxyethylene (**3b**) with aldehydes **4a–d** were carried out in water at room temperature in the presence of the surfactants **1a–b** (20 mol %) and the catalyst Sc(OTf)₃ (10 mol %) to afford the aldol adducts **5a–f** (eqs 2 and 3).



For comparison, the Sc(OTf)₃-catalyzed reactions in water were also examined with 20 mol % of the surfactant SDS (**2a**) instead of **1a–b**. The experimental results are summarized in Table 1. In the case of **2a**, the silyl enol ethers **3a–b** in the reaction mixture disappeared (as shown by TLC) after 1 h of reaction; however, a large amount of the aldehyde remained, leading to lower yields of the aldol products. In contrast, when surfactants **1a** and **1b** were used, the silyl enol ethers **3a** and **3b** were still present after a longer reaction time in aqueous solution. Presumably, the increased stability of the silyl enol ethers toward water

in the presence of **1a** and **1b** resulted in higher yields of the aldol products. The calix[6]arene derivative **1b**, having a hexyl group, exhibited an advantage over **1a**, which bears a shorter chain (butyl group), in both reaction rates and yields (a shorter reaction time and a higher yield). This difference can be explained by the fact that calix[6]arenes bearing alkyl groups on the lower rim can form a hydrophobic cavity that associates with the molecule of the silyl enol ether in water. This complex effectively shields the labile silyl enol ethers from hydrolysis and increases the concentration of silyl enol ethers in the hydrophobic reaction field. The size of the cavity formed by **1b** with a longer chain is larger and better accommodates the silyl enol ether molecule. Meanwhile, in the case of calix[4]arene **1d** (bearing a hexyl group on the lower rim), the reactions of **3a** with aldehydes **4a** and **4b** also gave the high yields (entries 4 and 11 in Table 1), similarly to the reaction in the presence of **1b**. On the other hand, in the presence of **1e** (bearing a dodecyl group on the lower rim), the reaction of **3a** with aldehyde gave a very small amount of aldol product, and a large amount of aldehyde was recovered after 20 h of stirring. The result was not surprising, as Shinkai et al. reported⁹ that the sulfonated calixarene bearing a dodecyl group on the lower rim does not have the surface-active feature.

Then, surfactants **1a–b** were examined for the aldol reactions of 1-phenyl-1-trimethylsiloxypropene (**3c**) (R² = Ph, R³ = CH₃) with aldehydes in water by the same experimental procedure (eq 4).



The results are summarized in Table 2. Because **3c** is relatively stable toward water, both the calix[6]arene surfactants **1a–b** and **2a** gave high yields of the aldol adducts **5g–k**. However, if a sulfonated calix[6]arene without alkyl groups on the lower rim (**1c**, R = H) was used instead of **1a–b**, the aldol reactions of **3c** with aldehydes did not proceed at all and **3c** was still present in the **1c**–Sc(OTf)₃–H₂O system even after 10 h of stirring. These results indicate that the alkyl group on the lower rim not only plays a role in stabilizing the silyl enol ethers but also promotes the aldol reaction in water. Compared to **1b**, **1a** is less effective in promoting the aldol reaction of **3c** (a longer reaction time) but gave a slightly higher diastereoselectivity (syn/anti) of the aldol products. This suggests that **1a**, having a shorter alkyl chain, results in a hydrophobic cavity that is too small to accommodate both substrates properly but is favorable for selectively hosting a substrate molecule. Thus, the calix[6]arene derivatives **1a–b** prove to be effective encapsulating surfactants for unstable silyl enol ethers in water, as well as being effective in promoting the Mukaiyama aldol reaction.

Encapsulating Effect of Aliphatic and Aromatic Anionic Surfactants. The effectiveness of the calix-

Table 1. Aldol Reactions of 3a–b with Aldehydes in Water Using 1a, 1b, 1d, and SDS (2a) as Surfactants

entry	aldehyde, R ¹	3, R ² R ³	surfactant	reaction time (h)	product	yield (%) (syn/anti)
1	4a , Ph	3a , (CH ₂) ₄	2a	1	5a	47 (72/28)
2			1a	7		88 (75/25)
3			1b	4		94 (77/23)
4			1d	2		94 (78/22)
5	4b , <i>p</i> -ClPh		2a	1	5b	74 (77/23)
6			1a	6		95 (78/28)
7			1b	3.5		96 (81/19)
8			2a	1		40 (61/39)
9	4c , <i>p</i> -CH ₃ OPh		1a	10	5c	63 (56/44)
10			1b	6		97 (67/33)
11			1d	2		86 (75/25)
12			2a	1		54 (52/48)
13	4d , PhCH=CH		1a	8	5d	75 (54/46)
14			1b	4		95 (57/43)
15			2a	1		34
16			1b	8		79
17	4e , <i>p</i> -NO ₂ Ph	3b , Ph H	2a	1	5f	68
18			1b	5		94

Table 2. Aldol Reaction of 3c with Aldehydes in Water Using 1a–b and 2a as Surfactants

entry	R ¹ CHO	surfactant	reaction time (h)	product	yield (%) (syn/anti)
1	4a	1a	8	5g	90 (31/69)
2		1b	3.5		92 (40/60)
3	4b	2a	2	5h	90 (40/60)
4		1a	6		95 (34/66)
5		1b	4		96 (40/60)
6		2a	2		93 (41/59)
7	4e	1a	5	5i	94 (20/80)
8		1b	4		96 (30/70)
9		2a	1.5		96 (30/70)
10		1a	6		90 (36/64)
11	4d	1b	4	5j	93 (49/51)
12		2a	3		92 (41/59)
13		1a	19		75 (38/62)
14	4f , CH ₃ (CH ₂) ₄	1b	9	5k	77 (43/57)
15		2a	4		65 (50/50)

[6]arene derivatives as encapsulating surfactants led us to study the factors contributing to such properties and to seek other surfactants exhibiting similar properties. In view of the molecular structure, the calix[6]arene derivatives **1a** and **1b** can be considered as bundles of aromatic anionic surfactants, whereas the less effective SDS is an aliphatic anionic surfactant. The dramatic difference between these two types of surfactants prompted us to investigate aromatic and aliphatic anionic surfactants for their encapsulating properties. For this investigation, the aliphatic anionic surfactants SDS (**2a**) and sodium dodecylsulfonate (**2b**) and the aromatic anionic surfactants sodium *p*-dodecyl sulfate (**2c**) and sodium *p*-dodecylphenyl sulfonate (**2d**) were used. The critical micelle concentrations (cmc's) of **2a**, **2b**, and **2d** are 8.1×10^{-3} , 9.8×10^{-3} , and 1.6×10^{-3} mol/L, respectively.⁹ The cmc of **2c** is not known but should be comparable to these values. Because of its relatively low stability, surfactant **2c** was freshly prepared by Scheme 1 and was used in the aqueous reaction immediately.

Reactions of **3a** with aldehydes **4a–d** (eq 1) in water at room temperature in the presence of the surfactants **2a–d** (20 mol %) and the catalyst Sc(OTf)₃ (10 mol %) were compared (Table 3). It was found that, in the presence of the alkyl sulfate surfactant **2a**, the silyl enol ether **3a** was unstable in water, leading to lower yields of aldol products (40–54%; entries 1, 5, 9, and 13 in Table 3). However, when the alkyl sulfate surfactant **2a** was replaced by the aryl sulfonate surfactant **2c**, the

yields of the aldol products were increased dramatically (88–99%; entries 3, 7, 11, and 14). For sodium alkyl and aryl sulfonates **2b** and **2d**, the same trend was observed: sodium alkyl sulfonate **2b** furnished lower yields (55–79%; entries 2, 6, and 10) and sodium aryl sulfonate **2d** higher yields (78–93%; entries 4, 8, and 12) of aldol products. The reactions of silyl enol ether **3b** with aldehydes **4a–b** were also carried out in water in the presence of the surfactants **2b** and **2d**. Again, a trend was noticed in which the yields of the aldol products **5e** and **5f** were lower for the aliphatic anionic surfactants than for the aromatic anionic surfactants under the same reaction conditions (entries 15 and 17 vs entries 16 and 18). It should be noted that no reaction was observed between **3b** and aldehydes in the absence of surfactants **2a–d**. Thus, it was tentatively suggested that micelles were formed in the presence of these surfactants and enabled the reactions to proceed smoothly. However, there was a competition between the hydrolysis of silicon substrate and the Mukaiyama aldol reaction. The rate of hydrolysis of the silicon substrates has a strong effect on the yield of the corresponding aldol reaction product. In the case of **2a** and **2b**, it was found that the silyl enol ethers **3a** and **3b** in the reaction mixture disappeared after 1 h of reaction, leading to lower yields of the aldol products. Thus, although labile silyl enol ethers can be stabilized by alkyl sulfates and sulfonates to some extent, hydrolysis of these ethers still occurs significantly in water. As control experiments, mixtures of silyl enol ether **3a** with **1c**, **1b**, **2b**, and **2d**, as well as solutions of **3a** without any surfactant, were stirred with Sc(OTf)₃ for 2 h in water. The reaction mixtures were then extracted with ether and analyzed by GC. The analysis showed that **3a** hydrolyzed to cyclohexanone completely with **2b** as the surfactant or without surfactant. On the other hand, mixtures with **1b**, **1c**, and **2d** as the surfactants revealed conversions of **3a** to cyclohexanone as 5, 44, and 80% respectively. These results show that the surfactants with aryl groups could inhibit the hydrolysis of labile silyl enol ethers and promote the aldol reactions more effectively than the aliphatic surfactants. It should also be noted that the yields of the reactions of **3a** with simple aliphatic aldehydes, such as nonyl aldehyde, in the presence of aromatic surfactant **2d** were very low (10%). The silyl enol ether **3a** disappeared within 0.5 h, generating a complicated mixture of products. Although, the exact reasons for the difference in effective-

Scheme 1

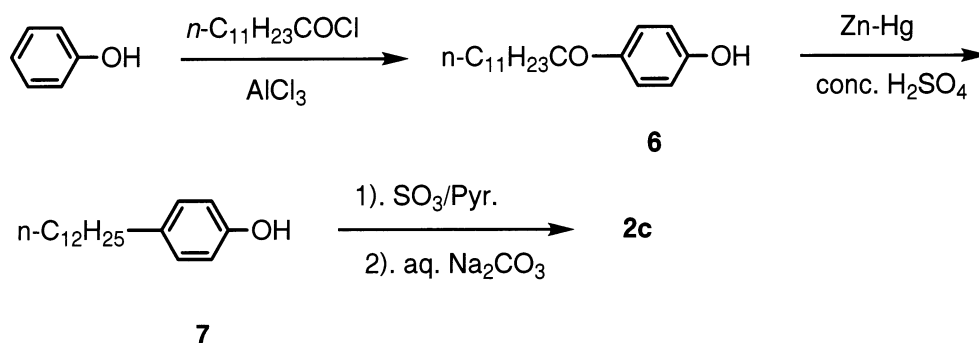


Table 3. Aqueous Aldol Reactions of 3a–b with Aldehydes in the Presence of Aliphatic and Aromatic Surfactants

entry	aldehyde, R	silyl enol ether	surfactant	reaction time (h)	product, R	yield ^a (%) (syn/anti)
1	4a, Ph	3a	2a	1	5a, Ph	47 (72/28)
2	4a	3a	2b	1	5a	55 (68/32)
3	4a	3a	2c	1	5a	99 (80/20)
4	4a	3a	2d	1	5a	85 (75/25)
5	4b, <i>p</i> -CH ₃ OPh	3a	2a	1.5	5b, <i>p</i> -CH ₃ OPh	40 (61/39)
6	4b	3a	2b	1.5	5b	61 (63/37)
7	4b	3a	2c	1.5	5b	98 (69/31)
8	4b	3a	2d	1.5	5b	93 (73/27)
9	4c, PhCH=CH	3a	2a	1	5c, PhCH=CH	54 (52/48)
10	4c	3a	2b	1	5c	70 (49/51)
11	4c	3a	2c	1	5c	88 (50/50)
12	4c	3a	2d	1	5c	78 (51/49)
13	4d, <i>p</i> -ClPh	3a	2a	1	5d, <i>p</i> -ClPh	74 (77/23)
14	4d	3a	2c	1	5d	98 (77/23)
15	4a	3b	2b	1	5e, Ph	49
16	4a	3b	2d	1	5e	61
17	4b	3b	2b	1	5f, <i>p</i> -CH ₃ O	43
18	4b	3b	2d	1	5f	58

^a Yields based on ¹H NMR data.

ness of the aliphatic and aromatic surfactants and for the difference in behavior of the aliphatic and aromatic aldehydes in the reaction are not clear, π – π interactions between the molecules of aryl surfactants and aryl aldehydes might play a role in these reactions. An alternative interpretation of the low yield for the reaction between 3a and nonyl aldehyde was that two micelle populations existed, one of which was stabilized by nonyl aldehyde (itself possibly serving as a surfactant) and the other of which was stabilized by 2d, thereby effectively keeping the two reactants in separate microenvironments.

In conclusion, amphiphilic calixarene derivatives 1a, 1b, and 1d, as well as aromatic anionic surfactants 2c–d, were able to encapsulate and stabilize water-sensitive compounds and reactive intermediates effectively in water, which allows the Sc(OTf)₃-catalyzed Mukaiyama reactions of labile enol silyl ethers with aldehydes to proceed in high yields in water. Further studies of the encapsulating mechanism and its synthetic applications are in progress.

Experimental Section

IR spectra were recorded on a Perkin-Elmer 782 infrared spectrometer. ¹H and ¹³C NMR spectra were measured on a Bruker DMX 300 spectrometer with tetramethylsilane as the internal standard. GC analysis was carried out on a Varian Vista 6000 gas chromatograph with a Supelco column (cyclohexane retention rate = 3.75 min, 3a retention rate = 4.04 min). Mass spectra (MS) were recorded on a KYKY-ZHT-5 spectrometer, FAB-MS on an AEIMS-50 spectrometer and

MALDI-TOF MS on a Bruker BIFLEX III spectrometer. Flash chromatography was performed on silica gel. All chemicals were reagent-grade and were used without further purification. Calix[6]arene derivatives 1a, 1b, 1d, and 1e were synthesized according to Shinkai's method.⁹

***p*-Dodecylphenyl Sulfate (2c).** To a stirred suspension of pyridine/sulfur trioxide complex (4.78 g, 30 mmol) in dry pyridine (15 mL) was added 7 (2.62 g, 10 mmol) in portions under nitrogen. Stirring was continued for 24 h at room temperature. After removal of the pyridine under reduced pressure, a saturated Na₂CO₃ solution was added. The insoluble white solid was collected by filtration, washed with ice-cold water, and dried under vacuum. The product was obtained as a white solid (2.66 g, yield 78%). ¹H NMR (D₂O): δ 0.72–(t, 3H, CH₃), 1.12 (m, 18H, CH₂), 1.35 (m, 2H, Ar–C–CH₂), 2.34 (t, 2H, Ar–CH₂), 6.96 (d, 2H, Ar–H), 7.09 (d, 2H, Ar–H). SIMS: 341.1796 (M⁺–Na) (calcd 341.1792).

General Procedure for the Aqueous Mukaiyama Aldol Reaction. To a mixture of surfactant (0.04 mmol) in water (1 mL) were added Sc(OTf)₃ (0.02 mmol), aldehyde (0.2 mmol), and silyl enol ether (0.3 mmol). The mixture was stirred at room temperature until the silyl enol ether disappeared on TLC. Then, the mixture was passed through a short silica gel pad and extracted with ethyl ether. The combined organic layer was dried over MgSO₄ and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired aldol adduct. All of the aldol products are known compounds, and their characterization data were consistent with the literature:

2-[hydroxy-(phenyl)methyl]cyclohexanone (**5a**),¹¹ 2-[hydroxy-(4-chlorophenyl)methyl]cyclohexanone (**5b**),¹¹ 2-[hydroxy-(4-methoxyphenyl)methyl]cyclohexanone (**5c**),¹² 2-(1-hydroxy-3-phenyl-2-propenyl)cyclohexanone (**5d**),¹³ 1,3-diphenyl-3-hydroxy-1-propanone (**5e**),¹⁴ 3-(4-nitrophenyl)-3-hydroxy-1-phenyl-1-propanone (**5f**),¹⁵ 3-(4-methoxyphenyl)-3-hydroxy-1-phenyl-1-propanone (**5m**),¹⁶ 1,3-diphenyl-3-hydroxy-2-methyl-1-propanone (**5g**),¹⁷ 3-(4'-chlorophenyl)-3-hydroxy-2-methyl-1-phenyl-1-propanone (**5h**),¹⁸ 1,5-diphenyl-3-hydroxy-2-methyl-4-pentene-1-one (**5i**),¹⁷ 3-hydroxy-2-methyl-1-phenyl-1-octanone (**5j**),¹¹ 3-(4-nitrophenyl)-3-hydroxy-2-methyl-1-phenyl-1-propanone (**5k**).¹⁹

Acknowledgment

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