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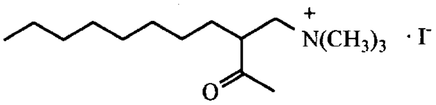
Preparation and Characterization of a Simple Destructible Surfactant

Craig A. West, Ana M. Sanchez, Karen A. Hanon-Aragon,
Idalia C. Salazar and Fredric M. Menger*

Department of Chemistry, Emory University, Atlanta, Georgia 30322

Abstract: A simple, two-step synthesis of (2-acetyldecyl)-trimethylammonium iodide, a base-labile surfactant, has been developed. Copyright © 1996 Elsevier Science Ltd

The utilization of surfactants in synthetic organic chemistry can often result in enhanced chemoselectivity, higher yields and milder reaction conditions.[1] However, one difficulty in employing surfactants is the formation of persistent emulsions, which can make reaction workup difficult. To counter this problem, several so-called destructible or cleavable surfactants have been reported.[2,3] These surfactants are designed to display normal aggregation behavior under certain conditions, but can be cleaved by acid- or base-hydrolysis[2] or by other chemical means.[3] Typically, the syntheses of compounds of this type require several steps. Herein, we report the synthesis and characterization of a base-labile destructible surfactant **1** that is prepared in two steps from commercially available starting materials.



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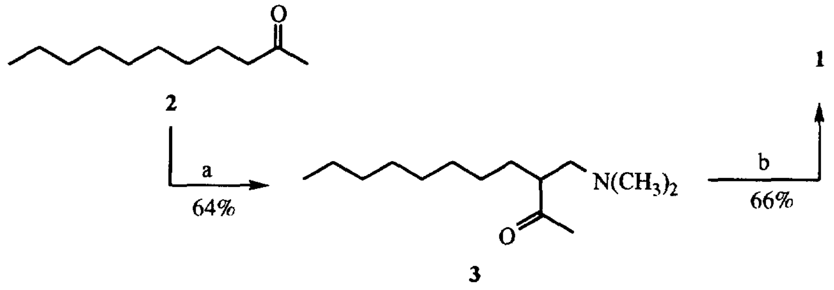
The preparation of surfactant **1** is detailed in Scheme 1. Conversion of ketone **2** to **3** was accomplished via a Mannich reaction[4,5], followed by quaternization of the tertiary amine with methyl iodide[6], yielding compound **1**. Both steps proceeded in moderate to good yield (Scheme 1). Synthetic details are provided at the end of the article.

Scheme 1



a) CH_2O, $(CH_3)_2NH{\cdot}HCl$, EtOH; b) MeI, CH_3CN

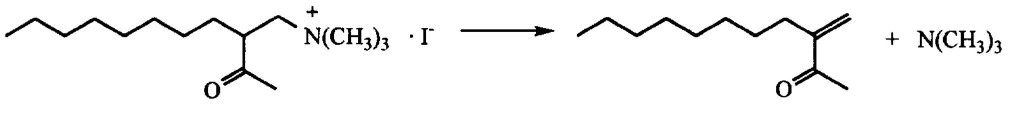
The critical micelle concentration (cmc) of surfactant **1** was determined by the Du Noüy (platinum ring) method[7] to be 2.5 x 10^{-2} M. Stability characteristics of surfactant **1** were examined by ^1H NMR spectroscopy and are summarized in Table 1. At 25 °C, surfactant 1 proved to be stable for extended periods of time in 0.01 M DCl (Entry 1). However, in neutral and basic media, the compound's behavior was quite different. It decomposed slowly in water (Entries 2-3), more rapidly in 0.1 M $NaHCO_3$ (Entries 4-5), rapidly in 0. 1 M Na_2CO_3 (Entries 6-7) and completely within 5 minutes in 0.1 M NaOD (Entry 8). The two decomposition products of **1** were identified by ^1H NMR (Scheme 2).[8] Percent decomposition of the

Table 1. Stability Characteristics of 0.05 M 1 in D_2O Solutions

	Additive	pH	Time	% Decomposition
1	0.01 M DCl	2.0	140 h	0
2	none	7.4	42 h	11
3	none	7.4	66 h	17
4	0.1 M $NaHCO_3$	8.2	6 h	20
5	0.1 M $NaHCO_3$	8.2	18 h	56
6	0.1 M Na_2CO_3	11.5	20 min	67
7	0.1 M Na_2CO_3	11.5	90	97
8	0.1 M NaOD	13.0	<5 min	100

surfactant was determined by comparing the area of the quaternary ammonium methyl peak of **1** with that of product trimethylamine .

Scheme 2



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In summary, surfactant **1** possesses aggregation properties of a typical quaternary ammonium surfactant, and undergoes base-catalyzed hydrolysis much in the same way as other base-labile surfactants previously reported by Jaeger and coworkers.[2d] Thus, surfactant **1** could be used to catalyze certain reactions, and subsequent base workup would convert **1** to non-surfactant products which can be readily removed. Moreover, the ease of preparation of surfactant **1** and the simplicity of the methodology makes this compound and perhaps longer chain analogs attractive reagents for use in preparative organic chemistry.[9]

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REFERENCES AND NOTES

1. For example, see: (a) Menger, F.M.; Rhee, J.U.; Rhee, H.K. *J. Org. Chem.* **1975**, *40*, 3803-3805. (b) Link, C.M.; Jansen, D.K.; Sukenik, C.N. *J. Am. Chem. Soc.* **1980**, *102*, 7798-7799. (c) Sutter, J.K.; Sukenik, C.N. *J. Org. Chem.* **1982**, *47*, 4174-4176.

2. (a) Jaeger, D.A.; Li, B.; Clark, T. *Langmuir*, **1996**, *12*, 4314-4316. (b) Jaeger, D.A.; Russell, S.G.G.; Shinozaki, H. *J. Org. Chem.* **1994**, *59*, 7544-7548. (c) Jaeger, D.A.; Finley, C.T.; Walter, M.R.; Martin, C.A. *J. Org. Chem.* **1986**, *51*, 3956-3959. (d) Jaeger, D.A.; Martin, C.A.; Golich, T.G. *J. Org. Chem.* **1984**, *49*, 4545-4547. (e) Jaeger, D.A. Ward, M.D. *J. Org. Chem.* **1982**, *47*, 2221-2223. (f) Cuomo, J.; Merrifield, J.H.; Keana, J.F.W. *J. Org. Chem.* **1980**, *45*, 4216-4219. (g) Keana, J.F.W.; Guzikowski, A.P.; Morat, C.; Volwerk, J.J. *J. Org. Chem.* **1983**, *48*, 2661-2666.

3. (a) Jaeger, D.A.; Ward, M.D.; Dutta, A.K. *J. Org. Chem.* **1988**, *53*, 1577-1580. (b) Dunkin, I.R.; Gittinger, A.; Sherrington, D.C.; Whittaker, P. *J. Chem. Soc., Chem. Commun.* **1994**, 2245-2246.

4. Blicke, F.F. *Org. React.* **1942**, *1*, 303-341.

5. A mixture of dimethylamine hydrochloride (2.66 g, 32.6 mmol), paraformaldehyde (1.02 g, 34.0 mmol), 2-undecanone (**2**, 4.30 g, 25 mmol) and concentrated HCl (200 µL) in 95% EtOH was refluxed for 2.5 hours under N_2. EtOH was removed under reduced pressure. The orange-yellow residue was then dissolved in CH_2Cl_2 and residual acid was removed by washing with saturated $NaHCO_3$. The aqueous phase was then

extracted with CH_2Cl_2 (3 x 25 mL). The combined organic layers were dried over anhyd. Na_2SO_4 and the solvent was removed by rotary evaporation. The mixture of product (R_f = 0.16, 19:1 MeOH/EtOAc) and starting material was separated by column chromatography on silica gel with 5% MeOH/EtOAc as eluent, which gave **3** as a clear oil (4.3 g, 64%): ^{1}H NMR (360 MHz, $CDCl_3$): δ 0.83 (t, 3H, $C\underline{H}_3(CH_2)_7$, 1.18-1.25 (m, 12H, $(CH_2)_6$), 1.28-1.55 (overlapping m, 2H), 2.10 (s, 3H), 2.18 (s, 6H, $N(CH_3)_2$), 2.53-2.66 (m, 3H) ; ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 14.01, 22.57, 27.37, 28.48, 29.14, 29.30, 29.62, 30.30, 31.76, 45.69, 51.67, 61.88, 212.08. IR (Neat) 2918 (s), 2858 (s), 2768 (s), 1708 (s), 1460 (s), 1352 (s), 1265 (s), 1224 (m), 1164 (m), 1115 (w), 1096 (w), 1040 (s), 950 (w), 920 (w), 837 (s), 721 (s) cm^{-1}; EI HRMS, calcd for 227.2249, found 227.2256.

6. To a solution of 2-acetyl-N,N'-dimethylaminodecane (496 mg, 2.18 mmol) in acetonitrile (3 mL) was added methyl iodide (11.4 g, 80.3 mmol). The reaction was sealed under Ar and vigorously stirred for 2 days. Acetonitrile and residual methyl iodide were then removed under reduced pressure, leaving a crude yellow solid that was triturated with anhyd. Et_2O (100 mL). The product was isolated as a white solid (529 mg, 66%): mp 117-118 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 0.85 (t, 3H, $C\underline{H}_3(CH_2)_7$), 1.18-1.26 (m, 12H, $(CH_2)_6$), 1.55-1.81 (overlapping m, 2H), 2.45 (s, 3H, CH_3CO), 3.38 (m, 1H), 3.41 (s, 9H, $N(CH_3)_3^+$), 3.74-3.81 (m, 1H), 4.01-4.08 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 13.96, 22.47, 26.07, 29.16, 29.19, 29.52, 29.57, 31.31, 31.73, 46.85, 54.18, 65.88, 208.11; IR (KBr) 2926 (s), 2851 (s), 1708 (s), 1468 (m), 1378 (m), 1359 (m), 1235 (m), 1168 (m), 1141 (m), 1119 (m), 968 (s), 908 (s), 781 (w), 721 (m), 600 (w), 503 (m) cm^{-1}; cmc = 2.5 x 10^{-2} M in distilled water at 25 °C; FAB HRMS, calcd for $C_{15}H_{32}NO$ (cation) 242.2484, found 242.2481; Anal. Calcd for $C_{15}H_{32}NOI$: C, 48.78; H, 8.73; N, 3.79. Found: C, 48.69; H, 8.71; N, 3.77.
7. Harkins, W.D.; Jordan, H.F. *J. Am. Chem. Soc.* **1930**, *52*, 1751.
8. Two products were observed by ^{1}H NMR in basic or neutral aqueous solutions: water soluble trimethylamine and a sparingly soluble organic liquid. The sparingly soluble product, 3-octyl-but-3-ene-2-one (**4**), was identified by ^{1}H NMR spectroscopy after extraction (3 x 10 mL Et_2O) of the combined Na_2CO_3 and NaOD solutions: (360 MHz, $CDCl_3$) δ 0.83 (t, 3H), 1.08-1.17 (m, 10H, $(CH_2)_5$), 1.20 (m, 2H), 2.11 (t, 2H), 2.16 (s, 3H, $CH_3C{=}O$), 5.76 (s, 1H, olefinic H), 6.01 (s, 1H, olefinic H). Other trace impurities were not identified.
9. An analog of **1**, with two additional methylenes in the chain, was found to decompose at a rate very similiar to that of **1**.

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