

prepared as above, and the mixture was stirred at 95–100 °C for 2 h 30 min. After the usual workup and chromatographic purification, the indole 11 was obtained: 83 mg (20%).

Method C. A solution of crude 1 phenylhydrazone (670 mg, 2.63 mmol) in freshly distilled 98–100% HCOOH (1 mL, 26.3 mmol) was refluxed for 1 h. After cooling, AcOEt (10 mL) was added, the mixture was made alkaline with saturated aqueous HNaCO₃ solution and extracted with AcOEt. Evaporation of the dried extracts gave a dark red oil (530 mg) which was chroma-

tographed as above to give the indole 11 (250 mg, 26%).

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Notes

An Expedient Synthesis of Bis(trimethylsilyl)carbodiimide

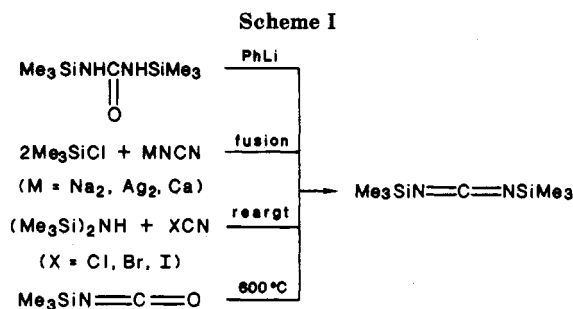
Khuong Mai* and Ghanshyam Patil

Section of Medicinal/Organic Chemistry, American Critical Care Division, American Hospital Supply Corporation, McGaw Park, Illinois 60085

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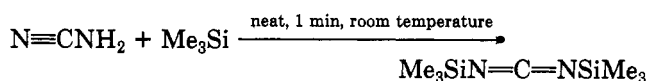
We have recently reported the preparation of a number of silylated compounds using alkylsilyl cyanides as silylating agents.¹ We now wish to describe an extension of this work involving the preparation of bis(trimethylsilyl)carbodiimide (BTMSC), which in turn is a very useful versatile synthetic intermediate.²⁻⁹

In general, BTMSC can be prepared either by the dehydration of bis(trimethylsilyl)urea,^{10,11} by the condensation of a metal cyanamide with trimethylsilyl chloride,¹²⁻¹⁵ by the reaction of hexamethyldisilazane with cyanogen halide followed by rearrangement,¹⁶ or by heating



trimethylsilyl isocyanate at 600 °C¹⁷ (Scheme I). Very recently, a patent was issued for the preparation of this carbodiimide.¹⁸

As seen in Scheme I, the reactions take place only under forcing conditions. We wish to report here that BTMSC can be prepared in 90% yield by the reaction of trimethylsilyl cyanide (Me₃SiCN) with cyanamide (eq 1). The reaction proceeds extremely fast and is complete within seconds. This is a pleasantly unexpected result since it has been reported that Me₃SiCN reacts with amines only at higher temperature (70 °C) and over prolonged periods of time (30 min).¹



Experimental Section

Bis(trimethylsilyl)carbodiimide. Performance of the reaction under an inert gas atmosphere is not necessary, but exposure of the reaction mixture or the product to moisture should be avoided.

In a well-ventilated hood, Me₃SiCN (12 g, 0.12 mol) was slowly added to cyanamide (2.1 g, 0.05 mol). A vigorous reaction was observed instantaneously as gaseous hydrogen cyanide was vented and trapped in a bottle containing caustic solution. After the exothermic reaction subsided (20 s), the homogeneous clear oil was distilled at atmospheric pressure to afford a colorless oil: yield, 11 g (91.7%); bp 158–162 °C; ¹H NMR (neat, with Me₃Si as internal standard) δ 0.18; IR spectrum indicates a very strong band typical for carbodiimide at 2190 cm⁻¹ (lit.¹⁰ bp 164 °C, IR 2190 cm⁻¹).

It should be noted that when only 1 equiv of Me₃SiCN was used, two clear layers were observed. Surprisingly enough, distillation also gave the bis(trimethylsilyl)carbodiimide in 80% yield instead of the expected *N*-mono(trimethylsilyl)cyanamide. Also after

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distillation, the bottom liquid layer solidified to an unidentified brown solid lump.

Registry No. N≡CNH₂, 420-04-2; Me₃SiCN, 7677-24-9; Me₃SiN=C=NSiMe₃, 1000-70-0.

Surfactant and Cation Effects on the Electrochemical Reduction of an α,β -Unsaturated Ketone

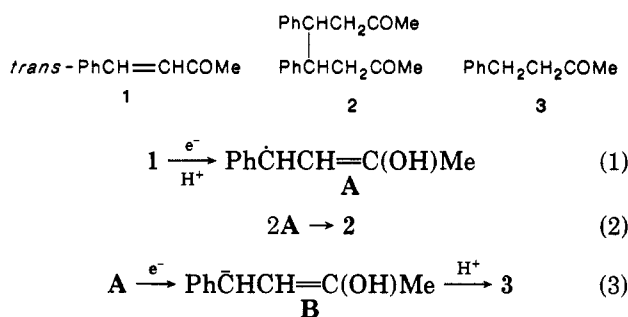
David A. Jaeger,* Durgadas Bolikal, and Buddhadeb Nath

Department of Chemistry, University of Wyoming, Laramie, Wyoming 82071

Received June 10, 1986

There have been numerous studies of surfactant effects on electrochemical reactions.¹ However, only a few have addressed synthetic applications.² Herein, we report the effects of surfactants and cations on the electrochemical reduction of α,β -unsaturated ketone **1** at a Hg cathode.

Ketone **1** has been electrochemically reduced previously under various conditions.³ For example, in 1:1 (v/v) EtOH-pH 5.1 NaOCOME-MeCO₂H buffer, its polarography gives two one-electron waves (I and II) with half-wave potentials ($E_{1/2}$) of -1.02 and -1.42 V, respectively,^{3a} and its electrolysis produces *meso*-**2** at -1.15 V and **2** and **3** at -1.55 V (vs. SCE).³ The first electron transfer is proton assisted³ and yields radical **A** (eq 1). Dimerization of **A**



gives **2** (eq 2), and its further reduction, **3**, through carbanion **B** (eq 3).⁴ Thus, even at potentials more cathodic than $E_{1/2}(\text{II})$, **2** is still formed.⁵ We have investigated the ability of surfactants and several cations to alter the partitioning of **A** between dimerization and further reduction.

The electrolysis of 0.010 M **1** and differential-pulse polarography of 1.0×10^{-4} M **1** in various media are summarized in Table I. In 1:1 (v/v) EtOH-pH 5.1 0.250 and

Table I. Electrolysis and Differential-Pulse Polarography of **1**

| entry | medium ^{a,b} | additive, 0.100 M | μ^c | yield, ^d % | | $-E_{1/2},^e$ V | |
|-----------------|--|----------------------|---------|--------------------------|----|-----------------|----------|
| | | | | 2 | 3 | I | II |
| 1 | 1:1 EtOH-H ₂ O (Na) | | 0.125 | 12 | 61 | 1.07 | 1.37 |
| 2 | 1:1 EtOH-H ₂ O (Na) | | 0.225 | 11 | 64 | 1.06 | 1.36 |
| 3 | 1:1 EtOH-H ₂ O (Na) | NaBr | 0.225 | 12 | 60 | 1.06 | 1.36 |
| 4 | 1:1 EtOH-H ₂ O (Na) ^f | NaBr | 0.225 | 17 | 60 | 0.96 | <i>g</i> |
| 5 ^h | 1:1 EtOH-H ₂ O (Na) | | 0.125 | 24 | 3 | | |
| 6 | 1:1 EtOH-H ₂ O (K) | KBr | 0.225 | 4 | 72 | 1.06 | 1.32 |
| 7 | 1:1 EtOH-H ₂ O (K) ⁱ | KBr | 0.225 | 5 | 76 | 1.19 | 1.30 |
| 8 | 1:1 EtOH-H ₂ O (Na) | Me ₄ NBr | 0.225 | 1 | 95 | 1.06 | 1.18 |
| 9 ^h | 1:1 EtOH-H ₂ O (Na) | Me ₄ NBr | 0.225 | 14 | 45 | | |
| 10 | 1:1 EtOH-H ₂ O (Na) | Bu ₄ NBr | 0.225 | 4 | 85 | 1.06 | 1.22 |
| 11 | 1:1 EtOH-H ₂ O (Na) | HTABr | 0.225 | 3 | 86 | 1.06 | <i>j</i> |
| 12 | 1:3 EtOH-H ₂ O (Na) | | 0.125 | 2 | 91 | 0.96 | 1.26 |
| 13 ^h | 1:3 EtOH-H ₂ O (Na) | Me ₄ NBr | 0.225 | 7 | 63 | 0.97 | 1.13 |
| 14 ^h | 1:3 EtOH-H ₂ O (Na) | HTABr | 0.225 | 1 | 97 | 1.01 | <i>k</i> |
| 15 | H ₂ O (Na) | | 0.250 | | | 0.92 | 1.21 |
| 16 | H ₂ O (Na) | NaBr | 0.350 | | | 0.91 | 1.18 |
| 17 | H ₂ O (Na) | Me ₄ NBr | 0.350 | | | 0.90 | 1.11 |
| 18 | H ₂ O (Na) | HTABr | 0.350 | 1 | 94 | 0.97 | 1.09 |
| 19 | H ₂ O (Na) | HTABr | 0.225 | 1 | 94 | | |
| 20 | H ₂ O (Na) ^f | HTABr | 0.225 | | | 0.88 | 1.11 |
| 21 ^h | H ₂ O (Na) | HTABr | 0.350 | 1 | 91 | | |
| 22 | H ₂ O (Na) | NaDodSO ₄ | 0.325 | 3 | 85 | <i>l</i> | 1.22 |
| 23 | H ₂ O (Na) | Brij 35 | 0.250 | 3 | 85 | 1.01 | 1.36 |

^a H₂O (Na) = NaOCOME-MeCO₂H buffer; H₂O (K) = KO-COME-MeCO₂H buffer in entry 6 and KH₂PO₄-K₂HPO₄ buffer in entry 7. The pH of the buffer before the addition of additive and/or EtOH, if used, was 5.1 unless noted otherwise; the ratio indicates v/v composition. ^b For differential-pulse polarography in entries 15-23, the medium contained 0.5% (v/v) EtOH. ^c For the solution as a whole. ^d From electrolysis of 0.010 M **1** at -1.55 V (vs. SCE) unless noted otherwise. ^e From differential-pulse polarography of 1.0×10^{-4} M **1**. ^f pH 3.5. ^g Only an ill-defined shoulder was observed at ca. -1.35 V. ^h Electrolysis at -1.275 V. ⁱ pH 7.0. ^j Only an ill-defined shoulder was observed at ca. -1.14 V. ^k Only an ill-defined shoulder was observed at ca. -1.09 V. ^l The peak was split into components at -0.96 and -0.99 V, presumably due to absorption of NaDodSO₄ on the electrode: Schmid, R. W.; Reilly, C. N. *J. Am. Chem. Soc.* 1958, 80, 2087.

0.450 M NaOCOME-MeCO₂H buffer (entries 1 and 2, respectively), and in the former with added 0.100 M NaBr (entry 3), the yield of **3** was essentially the same. Also, the same $E_{1/2}(\text{I})$ and $-E_{1/2}(\text{II})$ values were determined in entries 1-3. Thus, in these media with Na⁺ as the cation, the nature of the reduction does not depend on ionic strength over the range of total $\mu = 0.125$ -0.225. However, with the substitution of K⁺ for Na⁺ (entry 6), the yield of **3** increased, and $E_{1/2}(\text{II})$ underwent an anodic shift. Greater changes in the yield of **3** and $E_{1/2}(\text{II})$ were obtained when 0.100 M Me₄NBr, Bu₄NBr, and hexadecyltrimethylammonium bromide (HTABr) were added to the reaction mixture of entry 1 to give those of entries 8, 10, and 11, respectively. But note the invariance of $E_{1/2}(\text{I})$, which is consistent with the proton-assisted character of the first electron transfer³ and indicates that the shifts of $E_{1/2}(\text{II})$ are not due to double-layer effects derived from specific

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(5) Electrolysis of 0.01 M **1** at -1.55 V in 1:1 (v/v) EtOH-pH 5.1 NaOCOME-MeCO₂H buffer gave a coulometric *n* value of 1.58,^{3a} which corresponds to 42% and 58% yields of **2** and **3**, respectively, if only these compounds are formed.