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The reaction of carbamoylcopper with a silyl chloride to give a carbamoylsilane

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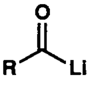
Abstract

A carbamoylsilane, $ArMeNCOSiMe_3$ (Ar = 2,6-dimethylphenyl) (**8**), is obtained in 54% yield by reacting trimethylsilyl chloride with lithium carbamoyl(cyano)cuprate (**7**). This was the product presumed to be formed by exposing a 1:1 mixture of CuCN and LiNMeAr to CO (1 atm) at 20°C.

Key words: Lithium; Silicon; Carbamoylsilane

1. Introduction

We have been developing methods of controlling carbonyl anions such as acyllithium **1** [1–3], a highly reactive species whose existence is only transient. The nitrogen analogue of acyllithium is known as carbamoyllithium **2** and it is known [4–6] to be more stable than acyllithium **1**. **2** has been shown to react with several electrophiles such as ketones to give addition products [5]. Consequently, it is expected that the reaction of **2** with a silylating reagent will give a carbamoylsilane **3**. However, this is not the case, as has been reported by Widdowson [7]. **3** was not obtained by the reaction of **2** with trialkylsilyl chlorides, even when a very bulky silyl chloride was included [7].



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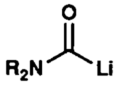

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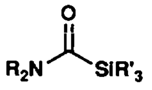

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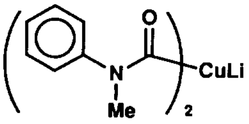
It seemed interesting and important to study further the reaction of the carbamoyl anion with silylating reagents, since only two compounds [8,9] (*vide infra*) with the structure of **3** have been reported to date. In this paper we report that the use of carbamoylcopper reagents [10–13] instead of **2** has led to satisfactory results.

2. Results and discussion

Since carbamoyl anions bearing lithium as the counter cation seemed unsuitable for the present purpose [7], we decided to study the reaction of carbamoyl anion in association with copper as the metallic species. Several reactions involving carbamoylcopper species are known. Tsuda reported that a 1:2 mixture of $LiNEt_2$ and CuCl reacted with CO (60 atm) at 180°C to give a diamide of oxalic acid [10]. Later, they found that lithium bis(diethylamino)cuprate, $LiCu(NEt_2)_2$, when reacted with CO (1 atm) and allyl bromide gave a carbamoylpropene by allylation of the carbamoyl anion [11]. The reaction gave a better yield when carried out under 50 atm of CO [11]. Wakita and co-workers studied the generation and methylation of carbamoylcopper from lithium *N*-methylphenylamide, CuI, and CO (1 atm) [12,13], and suggested the importance of cuprate **4** as an intermediate. These results indicated that the carbamoyl anion can be used in the form of cuprates. On the other hand, Seyferth reported a high yield transfer of "acyl anion" using a mixed cuprate derived from alkyllithium, CuCN and CO [14].



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We examined the reaction of a silyl chloride with a mixed cuprate derivable from a lithium amide, CuCN and CO, although the reaction of lithium amides with CuCN was not known [15,16]. The reaction did indeed give the desired carbamoylsilane **8** (eqn. (1)).

The reaction was carried out as follows (see Experimental section for details). The mixed cuprate **6**, prepared by adding 3.0 mmol of CuCN to a solution of 3.0 mmol of lithium *N*-methyl-2,6-dimethylphenylamide (**5**) in THF, was exposed to carbon monoxide at atmospheric pressure at 20°C for 8 h. Presuming the formation of a carbamoylcopper species **7**, the mixture was treated with 3.3 mmol of trimethylsilyl chloride and 4.0 mmol of TMEDA (tetramethylethylenediamine) at −78°C and warmed to 20°C. After workup with a sat. $NH_4Cl/10\%$ NH_4OH aqueous solution, the carbamoylsilane **8** was isolated in 54% yield by column chromatography on florisil (eqn. (1)). **8** is a white solid with m.p. 80–82°C which exhibited an IR absorption at 1576 cm^{-1} and a ^{13}C NMR signal at 188.3 ppm with $J(C\text{–}Si) = 75.0$ Hz for the carbonyl group. These and other analytical data are in accordance with those reported for diethylcarbamoyl(trimethyl)silane prepared by the reaction of bis(diethylcarbamoyl)mercury with bis(trimethylsilyl)sulfide [8] and for cyclohexylcarbamoyl(t-butyldiphenyl)silane obtained by the reaction of cyclohexyl isocyanate with t-butyldiphenylsilyllithium [9].

The reaction of the mixed cuprate with CO was also carried out under 30 atm of CO to give **8** in slightly higher yield (59%) (eqn. (1)). A similar homocuprate, lithium 2,6-dimethylphenyl(methyl)aminocuprate (**9**), prepared according to Tsuda's procedures in THF/HMPA (4:1), was reacted with CO (30 atm) for 3 h followed by quenching with Me_3SiCl and this also gave **8** in 35% yield (based on the two amide moiety) or 70% yield (assuming only one amide was reactive).

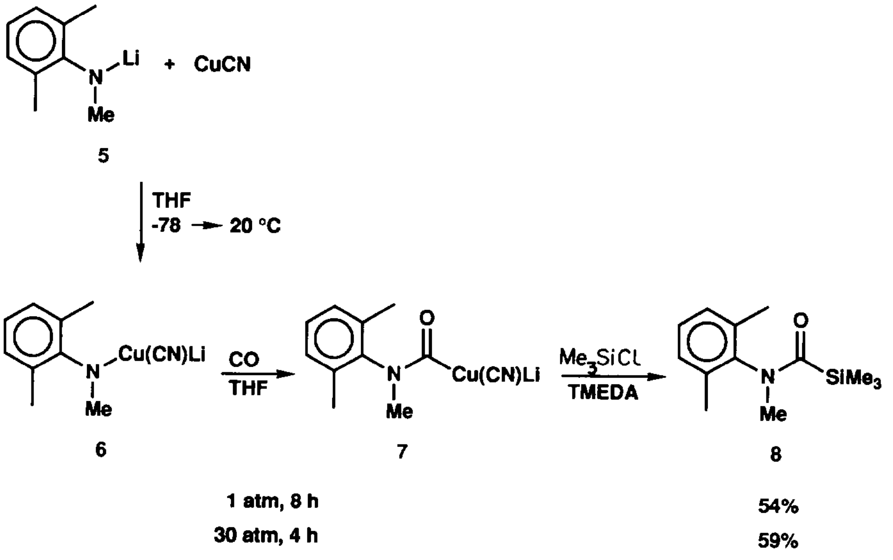
This shows that a carbamoylsilane such as **8** is relatively stable and can be manipulated in the usual manner. Encouraged by this observation we are examining the possibility of synthesizing carbamoylsilanes, a rare class of compounds, by an entirely different approach [17].

3. Experimental details

^1H NMR spectra were recorded with a JEOL JNM-GSX 270 (270 MHz) spectrometer as solutions in $CDCl_3$. IR spectra were recorded on a Hitachi 270-50 infrared spectrophotometer as KBr pellets or neat. Melting points were uncorrected. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. A hexane solution of n-BuLi (Nacalai Tesque, Inc.) was purchased and titrated prior to use by the Gilman method [18].

3.1. Synthesis of N-(2,6-dimethylphenyl)-N-(methyl)carbamoyl(trimethyl)silane (8) via a mixed cuprate 7

The reaction under 30 atm of CO was as follows. In a flame-dried glass flask equipped with a magnetic stirrer bar and a septum rubber, through which a short needle was connected to a nitrogen line, was placed anhydrous THF (5 ml) and *N*-methyl-2,6-dimethylaniline (0.406 g, 3.0 mmol) [19]. To the stirred solution was added dropwise by syringe a hexane solution of n-BuLi (2.2 ml, 1.35 M, 3.0 mmol) at −78°C. After 10



(1)

min, CuCN (0.269 g, 3.0 mmol) was added and the suspension was allowed to warm to 20°C over 1 h. After the removal of the nitrogen line from the short needle, the reaction vessel was quickly placed into an autoclave. The system was flushed and filled with a 30 atm pressure of carbon monoxide, and the mixture was stirred at 20°C for 4 h. After releasing the pressure of carbon monoxide, the glass vessel was taken out and a nitrogen line was reconnected to the short needle. To the reaction mixture was added dropwise trimethylsilyl chloride (0.42 ml, 3.3 mmol) and TMEDA (0.60 ml, 4.0 mmol) at −78°C. The mixture was allowed to warm gradually to 20°C. To the mixture was added a sat. $NH_4Cl/10\%\ NH_4OH$ aqueous solution (20 ml) and ether (10 ml). The organic layer and the aqueous layer were separated. The aqueous layer was extracted with ether (3×20 ml). The organic layers were combined, washed with brine, and dried over sodium sulfate. The solvents were removed under reduced pressure to give pale yellow solids, which were subjected to column chromatography on florisil (ether) to afford pure *N*-(2,6-dimethylphenyl)-*N*-(methyl)carbamoyl(trimethyl)silane (**8**) in 59% yield (0.416 g, 1.8 mmol).

3.1.1. N-(2,6-Dimethylphenyl)-N-(methyl)carbamoyl(trimethyl)silane (8)

A white solid, m.p. 80–82°C. ^1H NMR ($CDCl_3$): $\delta -0.14$ (s, 9H, CH_3Si), 2.20 (s, 6H, CH_3), 3.10 (s, 3H, CH_3N), 7.10 (d, $J = 8.8$ Hz, 1H, *m*-H), 7.11 (d, $J = 5.5$ Hz, 1H, *m*-H), 7.18 (dd, $J = 8.8$, 5.5 Hz, 1H, *p*-H). ^{13}C NMR ($CDCl_3$): $\delta -1.6$ (CH_3Si), 17.8 (CH_3), 32.8 (CH_3N), 128.4 (*p*-C), 128.6 (*m*-C), 137.3 (*o*-C), 141.0 (*i*-C), 188.3 (C=O, $J(C\text{–}Si) = 75.0$ Hz). ^{29}Si NMR ($CDCl_3$): $\delta -9.0$. IR (KBr): 1576 (C=O) cm^{-1}. MS *m/z* (relative intensity) 236 (22), 235 (M^+, 98), 73 (100). Anal. Calcd for $C_{13}H_{21}NOSi$: C, 66.33; H, 8.99; N, 5.95. Found: C, 66.49; H, 9.09; N, 5.95%.

The reaction under 1 atm of CO was carried out essentially in the same manner as described above but using a CO balloon.

3.2. Reaction giving 8 via a homocuprate, lithium bis(carbamoyl)cuprate 9

To a THF (6 ml) and HMPA (1.5 ml) solution of lithium amide (prepared from 4.0 mmol of *N*-methyl-2,6-dimethylaniline and 4.0 mmol of n-BuLi) was added CuCl (0.198 g, 2.0 mmol) at −20°C. The suspension was allowed to warm to 20°C over 1 h. The suspension was exposed to CO at 30 atm in a similar manner as described above and stirred for 3 h. After releasing CO, to the reaction mixture was added dropwise trimethylsilyl chloride (0.51 ml, 4.0 mmol) at −78°C. Successive aqueous workup, extraction with ether, drying with magnesium sulfate, and concentration gave a yellow liquid, which was subjected to column chromatography to afford pure *N*-(2,6-dimethylphenyl)-*N*-(methyl)carbamoyl(trimethyl)silane (**8**) (0.328 g, 1.4 mmol): for yields see text.

Acknowledgments

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