*Journal of Organometallic Chemistry*, 117 (1976) 149—155

# CHEMISTRY OF ORGANOSILICON COMPOUNDS

# XC *. THE REACTION OF THE TRIMETHYLCHLOROSILANE—LITHIUM—ALIPHATIC KETONE MIXTURE IN 1,3-DIMETHYL-2-IMIDAZOLIDINONE

HIDEKI SAKURAI * and FUMIHIKO KONDO
*Department of Chemistry, Faculty of Science, Tohoku University,Sendai 980 (Japan)*
(Received March 15th, 1976)

## Summary

The reaction of a trialkylchlorosilane with lithium in 1,3-dimethyl-2-imidazolidinone (DMI) at room temperature afforded the corresponding hexaalkyldisilane in good yield. The reaction of the mixture of trimethylchlorosilane and lithium with aliphatic ketones such as cyclohexanone and 3-pentanone gave doubly-silylated compounds in 30—40% yield. The character of DMI as an aprotic basic solvent is in between THF and HMPA and may be very useful as a new solvent for organometallic reactions.

## Introduction

In a previous paper [1] we have demonstrated that 1,3-dimethyl-2-imidazolidinone (DMI) is sufficiently basic and stable for the preparation of trimethylsilylsodium, one of the strongest bases. It is known that, except for HMPA, common aprotic dipolar solvents such as DMF [2], DMSO [3], and tetramethylurea [4] are rather reactive towards a strong base and alkali metals. Therefore, being stable towards alkali metals, DMI is expected to be a useful solvent in a variety of reactions. In this paper we describe briefly some reactions of lithium metal in DMI which may demonstrate the usefulness of DMI as a solvent for organometallic reactions.

## Results and discussion

*The reaction of $R_3SiCl$ and Li.* The reaction of trimethylchlorosilane with an equimolar quantity of lithium in DMI afforded hexamethyldisilane in 95% yield

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* For part LXXXIX see ref. 12.

under the conditions outlined in eq. 1:

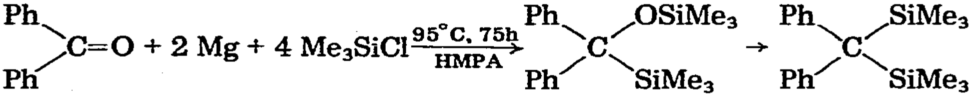
$$2\ Me_3SiCl + 2\ Li \xrightarrow[43\ h]{room\ temp.} Me_3SiSiMe_3 + 2LiCl \qquad (1)$$

Similarly, hexaethyldisilane was prepared by the coupling reaction of triethylchlorosilane with an equimolar quantity of lithium in DMI in 52.4% yield. Coupling of triethylchlorosilane is less efficient, but the yield was improved to 61.7—76.7%, if two molar excess lithium was used. Therefore, these findings provide another convenient method of preparing hexaalkyldisilanes. Gilman et al. [5] reported that hexaalkyldisilanes could be prepared from trialkylchlorosilane and lithium metal in THF. However, the reaction reportedly requires vigorous stirring by a special stirrer with lithium sands. Recently, we have found that hexaalkyldisilane was obtained in high yield from the reaction of trialkylchlorosilane and alkali metals such as sodium and lithium in ether or THF containing an equimolar amount of HMPA to trialkylchlorosilane [6]. However, when HMPA alone was used as a solvent, only hexamethyldisiloxane was obtained and formation of hexamethyldisilane was not observed (eq. 2).

$$2\ Me_3SiCl + 2\ Li \xrightarrow{HMPA} Me_3SiOSiMe_3 + 2\ LiCl \qquad (2)$$

These facts suggest that DMI is more stable than HMPA in the reaction of trimethylchlorosilane and lithium. Therefore, DMI should be very useful as a solvent for organometallic reactions. This was demonstrated further in the silylation of saturated ketones with trimethylchlorosilane and lithium in DMI.

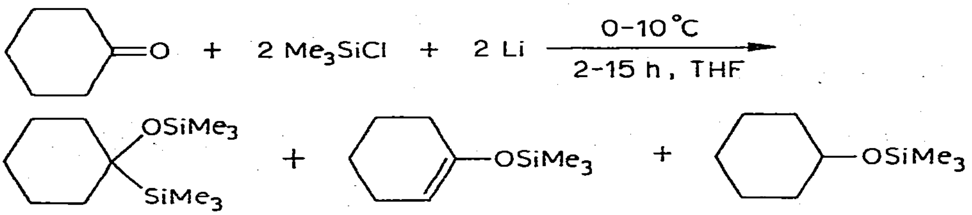
*The reaction of Me₃SiCl/Li with ketones.* The double silylation of aryl ketones with trimethylchlorosilane and magnesium in HMPA was reported first by Calas et al. and extended to syntheses of various organosilicon compounds [7]. However, this type of double silylation requires rather vigorous reaction conditions, and moreover, it has been reported that the reaction can only be applied successfully to aryl ketones (eq. 3).



(3)

(65%)

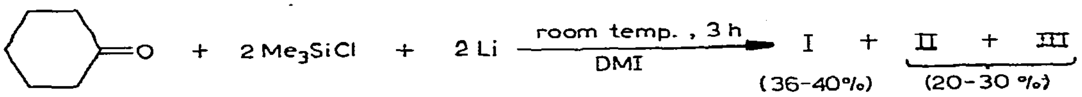
Recently, Calas et al. [8] reported double silylation of a saturated ketone with trimethylchlorosilane and lithium in THF, although yields of the corresponding doubly-silylated products are rather low. For example, 1-trimethylsilyl-1-trimethylsiloxycyclohexane (I, 12%), cyclohex-1-enoxytrimethylsilane (II, 46%) and cyclohexyloxytrimethylsilane (III, 17%) were obtained from cyclohexanone (eq. 4).



(4)

(I) (II) (III)

We have found that DMI can be successfully applied to double silylation of aliphatic ketones. Thus, the reaction of cyclohexanone with trimethylchlorosilane and lithium in DMI afforded I in 36—40% yield in addition to II and III in 20—30% yield under the conditions outlined in eq. 5.



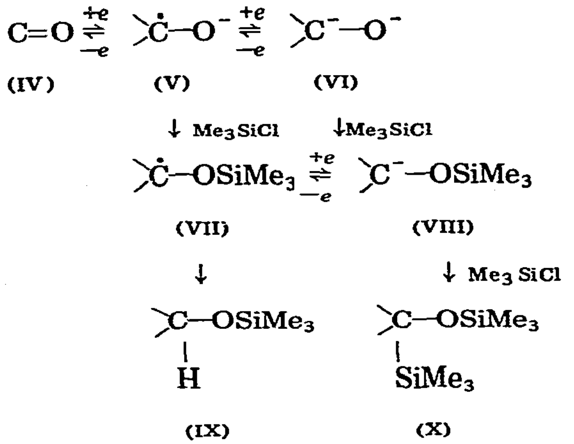
(5)

Similarly, diethyl ketone and methyl isopropyl ketone afforded 3-trimethylsilyl-3-trimethylsiloxypentane and 2-trimethylsilyl-2-trimethylsiloxy-3-methylbutane in 39.6 and 34.4% yields, respectively, by treatment with trimethylchlorosilane and lithium in DMI. The reaction of methyl n-hexyl ketone afforded 2-trimethylsilyl-2-trimethylsiloxyoctane in 26.0% yield under the same conditions.

These findings suggest that a bulky substituent such as n-hexyl and isopropyl groups on the carbonyl group retards the double silylation. This may be ascribed to the fact that electron transfer from lithium metal to the ketones and/or the attack of the anion produced by electron transfer to the ketones are sterically hindered by these bulky substituents on the carbonyl group.

The double silylation reaction of ketones may be rationalized by Scheme 1 [8].

SCHEME 1



The ketyl radical V is formed by transfer of one electron from lithium metal to the ketone, and reacts with trimethylchlorosilane to give a siloxy radical (VIII). The doubly silylated product X arises from the reaction of a siloxycarbanion (VIII), formed from either the dianion VI or electron transfer to the siloxy radical VII, with trimethylchlorosilane, although the intermediacy of VI seems unlikely in the aliphatic system. The radical VII may be converted to the alkoxysilane IX by hydrogen abstraction. According to Scheme 1 the ratio of X to IX may be determined by the relative rate of electron transfer to VII versus hydrogen abstraction from the solvent.

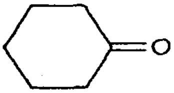
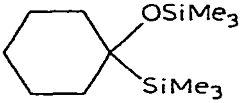
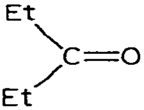
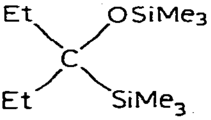
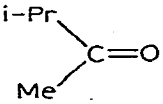
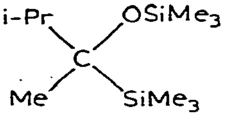
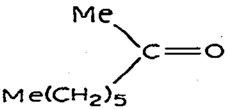
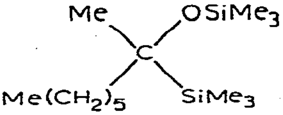
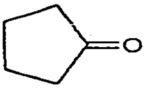
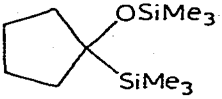
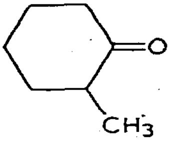
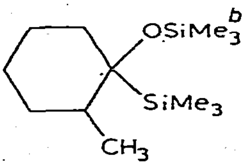
The ratio of the alkoxysilane IX to the doubly-silylated compound X is larger in THF than that in DMI. This fact may be explained by the favorable electron transfer from lithium metal to VII in DMI. As a result, the doubly-silylated product may be formed more favorably in DMI than in THF. Finally, double silylations of other aliphatic ketones such as 2-methylcyclohexanone and cyclopentanone have also been attempted and are found to give the corresponding doubly-silylated products. The results are listed in Table 1.

## Experimental

Infrared spectra were recorded on a Hitachi EPI-S spectrometer and $^1$H NMR spectra were taken on a Varian A-60 (partly on a Varian T-60 spectrometer). GLC analyses were carried out on a Hitachi K-53 gas chromatograph. n-Octane (O), n-nonane (N), n-undecane (U) and n-tridecane (T) were used as internal standards.

TABLE 1

DOUBLE SILYLATION OF KETONES

| | | |
|---|---|---|
|  |  | (36–40) |
|  |  | (39·6) |
|  |  | (34·4) |
|  |  | (26·0) |
|  |  | (17·2) |
|  |  | (36·6) |

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[a] Yields are determined by GLC (see Experimental). [b] Only the single isomer was obtained.

### *Materials*

2-Imidazolidinone(ethyleneurea), trimethylchlorosilane and lithium are commercially available chemicals. 2-Imidazolidinone was also prepared by the known procedure [9]. Triethylchlorosilane was prepared from tetraethylsilane as reported previously [10].

### *Preparation of 1,3-dimethyl-2-imidazolidinone (DMI) [11]*

In a 500 ml flask, fitted with a reflux condenser and a thermometer were placed 43 g (0.50 mol) of 2-imidazolidinone, 90% formic acid (135.4 g, 1.50 mol) and 35% formaldehyde (113.5 g). The solution was heated for 44 h at 100—110°C. After the solution was cooled, 4 *N* hydrochloric acid (250 ml) was added and the solution was evaporated to dryness under reduced pressure with a suction pump on a water bath. A deep reddish, syrupy residue was dissolved in 125 ml of water and DMI was liberated by adding an 18 *N* sodium hydroxide solution (130 ml). The upper layer was separated and then the lower aqueous layer was extracted with 200 ml of chloroform. DMI and chloroform extracts were combined and dried over calcium chloride. After chloroform was distilled, DMI was distilled under reduced pressure to give a colorless liquid (44.1 g, 77%), b.p. 104°C/18 mmHg, $n^{20}$1.4709 (lit.[11], $n^{26}$ 1.4700). Anal. Found: C, 52.88; H, 8.95; N, 24.56. $C_5H_{10}ON_2$ calcd.: C, 52.61; H, 8.83; N, 24.54%.

### *Preparation of hexamethyldisilane*

To a 100 ml three-necked flask equipped with a reflux condenser and a dropping funnel were placed lithium chips (0.14 g, 20 mmol) and DMI (8 ml). After a solution of trimethylchlorosilane (2.17 g, 20 mmol) and n-octane (0.45 g, 3.97 mmol, an internal standard for GLC analysis) in DMI (2 ml) was added, the reaction mixture was stirred at 22°C for 43 h. The solution was hydrolyzed and the mixture was extracted with diethyl ether. Hexamethyldisilane was afforded in 95.0% yield (GLC). The product was distilled and purified by preparative GLC. The product was identified by comparison of the IR spectrum with that of an authentic sample.

### *Preparation of hexaethyldisilane*

In the same manner, hexaethyldisilane was prepared from triethylchlorosilane (3.01 g, 20 mmol) and lithium (0.14 g, 20 mmol) in DMI (10 ml) in 52.4% yield (GLC; U, 3.29 mmol). The reaction mixture was stirred at 19°C for 6 h.

When excess lithium (0.14 g, 20 mmol) was used with triethylchlorosilane (1.50 g, 10 mmol), yields improved to 61.7—76.7% under the same conditions.

### *Double silylation of diethyl ketone in DMI*

The experimental procedure of diethyl ketone is described as a typical example. In a 100 ml three-necked flask equipped with a reflux condenser, a dropping funnel, a stirring bar and lithium chips (0.17 g, 25 mmol) and DMI (10 ml) were placed. The dropping funnel was filled with a mixture of trimethylchlorosilane (3.26 g, 30 mmol), diethyl ketone (0.86 g, 10 mmol), and n-tridecane (0.42 g, 2.26 mmol, an internal standard for GLC) in DMI (10 ml). After the flask was filled with dry argon, the solution of the substrates was added drop by drop to lithium chips. After addition was complete, the mixture was stirred at ambient temperature (19° C) for 3 h. The solution was then hydrolyzed with water (60 ml) and extracted with diethyl ether (80 ml). DMI in the ethereal layer was removed by shaking with water (40 ml) and the ethereal layer was dried over anhydrous sodium sulfate. The yield of 3-trimethylsilyl-3-trimethylsiloxypentane was determined by GLC to be 39.6%. The product was distilled and purified by preparative GLC, NMR ($\delta(CCl_4)$ppm) 1.66(q, 4H, $CH_2$), 0.89(t, 6H, $CH_3$), 0.10 and 0.03 (s, 18H, $2SiMe_3$); IR ($cm^{-1}$, neat) 1250($SiMe_3$), 1055-(C—$OSiMe_3$), and 835($SiMe_3$), (lit. [8] NMR ($\delta(CCl_4)$ppm) 1.75(q, 4H, $CH_2$), 0.95(t, 6H, $CH_3$), 0.2 and 0.1(s, 18H, $2SiMe_3$); IR ($cm^{-1}$, neat) 1060(C—$OSiMe_3$)). Anal. Found: C, 56.80; H, 12.10. $C_{11}H_{28}OSi$ calcd.: C, 56.82; H, 12.14%.

*1-Trimethylsilyl-1-trimethylsiloxycyclohexane*

1-Trimethylsilyl-1-trimethylsiloxycyclohexane was obtained in 40.8% yield (GLC; O, 3.30 mmol) by the reaction of cyclohexanone (0.98 g, 10 mmol), trimethylchlorosilane (3.26 g, 30 mmol) and lithium (0.17 g, 25 mmol) at 19° C for 3 h in DMI, NMR ($\delta(CCl_4)$ppm) 2.10—1.70 (m, 10H, cyclic $CH_2$), 0.14(s, 9H, O—$SiMe_3$) and 0.00(S, 9H, C—$SiMe_3$); IR ($cm^{-1}$, neat) 1250($SiMe_3$), 1060-(C—$OSiMe_3$) and 830($SiMe_3$), (lit. [8], IR ($cm^{-1}$, neat) 1065(C—$OSiMe_3$)). Anal. Found: C, 58.89, H, 11.44. $C_{12}H_{28}OSi_2$ calcd.: C, 58.94; H, 11.54%.

*2-Trimethylsilyl-2-trimethylsiloxy-3-methylbutane*

2-Trimethylsilyl-2-trimethylsiloxy-3-methylbutane was obtained in 34.4% yield (GLC; T, 1.83 mmol) by the reaction of isopropyl methyl ketone (0.86 g, 10 mmol), trimethylchlorosilane (3.26 g, 30 mmol) and lithium (0.17 g, 25 mmol) in DMI (15 ml), NMR ($\delta(CCl_4)$ppm) 1.26(s, 3H, $CH_3$), 0.95(d, 7H, i-Pr), 0.17 and 0.07(s, 18H, $2SiMe_3$); IR($cm^{-1}$, neat) 1253($SiMe_3$), 1060(C—$OSiMe_3$) and 836($SiMe_3$). Anal. Found: C, 56.96; H, 12.15. $C_{11}H_{28}OSi_2$ calcd.: C, 56.82; H, 12.14%.

*2-Trimethyl-2-trimethylsiloxyoctane*

2-Trimethylsilyl-2-trimethylsiloxyoctane was obtained by the reaction of 2-octanone (1.28 g, 10 mmol), trimethylchlorosilane (3.26 g, 30 mmol) and lithium (0.17 g, 25 mmol) at 19° C for 2 h in 26.0% yield (GLC; 3.44 mmol), NMR ($\delta(CCl_4)$ppm) 1.23(m, 13H, s, 3,4,5,6,7-$CH_2$, 8-$CH_3$), 0.87(m, 3H, 1-$CH_3$), 0.00 and —0.12(s, 18H, $2SiMe_3$); IR ($cm^{-1}$, neat) 1255($SiMe_3$), 1060(C—$OSiMe_3$), and 835($SiMe_3$). Anal. Found: C, 61.19; H, 12.52. $C_{14}H_{26}OSi_2$ calcd.: C, 61.24; H, 12.48%.

*1-Trimethylsilyl-1-trimethylsiloxy-2-methylcyclohexane*

1-Trimethylsilyl-1-trimethylsiloxy-2-methylcyclohexane was obtained similarly from 2-methylcyclohexanone (1.12 g, 10 mmol),trimethylchlorosilane (3.26 g, 30 mmol) and lithium (0.17 g, 25 mmol) in DMI (15 ml) in 36.6% yield (GLC; O, 3.55 mmol), NMR ($\delta(CCl_4)$ppm) 1.42(m, 9H, 2-CH, 3,4,5,6-$CH_2$), 1.00(d, 3H, 2-$CH_3$), 0.08 and 0.05 (s, 18H, $2SiMe_3$). Anal. Found: C, 60.20; H, 11.66. $C_{13}H_{30}OSi_2$ calcd.: C, 60.39; H, 11.70%. Judging from GLC and spectral data, the compound was obtained as a single isomer of the two possible structures, but the stereochemistry has not been determined yet.

### *1-Trimethylsilyl-1-trimethylsiloxypentane*

1-Trimethylsilyl-1-trimethylsiloxypentane was obtained in 17.2% yield (GLC; T, 1.68 mmol) by the reaction of cyclopentanone (0.84 g, 10 mmol), trimethylchlorosilane (3.26 g, 30 mmol) and lithium (0.17 g, 25 mmol) in DMI (15 ml), NMR ($\delta$($CCl_4$)ppm) 1.60(s, 8H, cyclic-$CH_2$), —0.03 and —0.10(s, 18H, 2$SiMe_3$); IR (cm$^{-1}$, neat) 1234($SiMe_3$), 1048(C—$OSiMe_3$) and 820($SiMe_3$). Anal. Found: C, 57.57; H, 11.38%. $C_{11}H_{26}OSi_2$ calcd.: C, 57.32; H, 11.37.

## Acknowledgment

We thank Toshiba Silicone Co., Ltd., for a gift of chlorosilanes.

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