Journal of Organometallic Chemistry, 363 (1989) 1–5
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 09560

Improved synthetic route to potassium silyl using crown ethers, potassium, and silane and its use to prepare methylsilane and disilylmethane

Benjamin F. Fieselmann * **and C. Robert Dickson**
Solarex Corporation, Thin Film Division, Newtown, PA 18940 (U.S.A.)

(Received April 18th, 1988; in revised form July 29th, 1988)

Abstract

The time for the reaction between K and SiH_4 in glyme is reduced from months to hours by addition of 18-crown-6 to form [K(18-crown-6)]SiH_3. The usefulness of the reaction to prepare the SiH_3^- anion as a synthetic intermediate is demonstrated by the reaction of [K(18-crown-6)]SiH_3 with CH_3I and CH_2Cl_2 to prepare H_3SiCH_3 and $(H_3Si)_2CH_2$, respectively. The rate of the reaction between K and GeH_4 is also increased but not as dramatically with the addition of 18-crown-6 to form [K(18-crown-6)]GeH_3.

Introduction

Interest in rapidly and conveniently generating silyl (SiH_3^-) anions arises from a need to prepare organosilane compounds of the form $(SiH_3)_nCH_{(4-n)}$, where $n = 1$–4. These compounds are useful as feedstocks to incorporate carbon during plasma deposition of amorphous silicon carbide and other silicon/carbon containing materials [1]. Compounds which contain several SiH_3 groups provide the potential to build in functionality such as Si–C–Si bonds, which may remain in the amorphous silicon after plasma deposition. Finally, H_3SiCH_3 and related compounds can be used as starting materials for the synthesis of more complex carbosilanes [2].

The silyl (SiH_3^-) and germyl (GeH_3^-) anions are useful synthetic intermediates that react with alkyl halides to introduce the SiH_3 or GeH_3 functional groups as shown in eq. 1 and 2 [3], where X = Cl, Br, or I and R = an alkyl group.

$$KSiH_3 + RX \rightarrow RSiH_3 + KX \qquad (1)$$

$$KGeH_3 + RX \rightarrow RGeH_3 + KX \qquad (2)$$

The GeH_3^- anion can readily be prepared from the reaction of GeH_4 in ether solvents with alkali metals (eq. 3) or KOH (eq. 4) [4,5], where M = Li, Na, K, Rb, or Cs.

$$M + GeH_4 \rightarrow MGeH_3 + 0.5H_2 \tag{3}$$

$$2KOH + GeH_4 \rightarrow KGeH_3 + KOH\ H_2O \tag{4}$$

Because SiH_4 is much less reactive than GeH_4 with alkali metals in polyether solvents, the preparation of $KSiH_3$ from K and SiH_4 requires a long time (over a month) [6,7]. This long reaction time greatly reduces the synthetic usefulness of the SiH_3^- anion. Other synthetic procedures such as using sodium/potassium alloys, employing the solvent hexamethylphosphoramide (HMPA), and starting with Si_2H_6 have been reported in preparing $KSiH_3$, but the alternate routes are either slow or introduce other synthetic difficulties [7–10].

Experimental

General procedure and material. Gas sample manipulations were carried out using a standard vacuum line fitted with O-ring connectors (9 mm ID) held together by pinch clamps with screwlocks (Kontes). Reactions were run in 250 and 500 ml vacuum storage bulbs (Kontes) modified with O-rings connectors to replace the original ground glass joints. Glyme (ethylene glycol dimethyl ether, anhydrous, 99%), methylene chloride (anhydrous, 99 + %), and 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane, 99%), were purchased from Aldrich. Glyme was purified by distillation over nitrogen from Na/benzophenone. Silane (SiH_4; CCD grade, 99.98%) was purchased from Airco and GeH_4 (99.99%) was obtained from Matheson. Potassium (as sticks) was obtained from Alfa Products.

Gas analyses were carried out on a Hewlett Packard gas chromatograph (5890)/mass spectrometer (5970) using a 10 cm^3 loop gas injection system and a 6ft. × 0.125 in. stainless steel analytical column packed with Porapack PSAW (Supelco). Quantitative analyses were made using a Tracor ultrasonic detector and a Shimadzu C-R3A integrator/recorder. After entering the ultrasonic detector the sample was sent directly into a jet separator (SGE) and then into the mass spectrometer.

Synthesis. The compounds prepared were air sensitive so synthetic work was carried out to prevent contact with air or moisture. The crown ethers and GeH_4 are toxic. *Silane is pyrophoric and explosive if brought in contact with air. All synthetic work with silane is dangerous and appropriate safety precautions should be taken.*

All vacuum connections were checked to ensure that they had sealed properly. All SiH_4 reactions were carried out behind safety shields. The following are sample descriptions of numerous reactions carried out:

Methylsilane (H_3SiCH_3). Freshly distilled glyme (7 ml) and 1.9 g (7.2 mmol) of 18-crown-6 were added to a 250 ml vacuum storage bulb filled with nitrogen. Potassium metal (0.23 g, 5.9 mmol) in small pieces (each less than 0.05 g) and a magnetic stir bar were added to the bulb under nitrogen. The solution turned dark blue as the potassium dissolved. The reaction bulb was cooled with liquid nitrogen, and the nitrogen atmosphere was pumped away. Silane (5.1 mmol) was condensed onto the frozen solution. After warming to room temperature, the solution turned light green as the reaction was stirred for 3 h and a white precipitate of [K(18-crown-6)SiH_3 formed. The bulb was cooled with liquid nitrogen and 2.5 mmole

(87% of the theoretical amount) of H_2 was obtained based on GC analyses and the pressure of H_2 in a calibrated volume. Upon warming, the H_2, solvent, and unreacted SiH_4 were removed in vacuo. The reaction vessel was cooled with liquid nitrogen. Methyl iodide (1.1 g, 7.75 mmol) was condensed onto the frozen material and the mixture was warmed to −38 °C over 2 h. The product gases, removed and analyzed by GC/MS, consisted of H_3SiCH_3 (3.25 mmoles, yield of 64%), SiH_4 (0.8 mmol), CH_3I (0.5 mmol), and traces of CH_4 and C_2H_6 (less than 0.1 mmol of each).

Disilylmethane [$(H_3Si)_2CH_2$]. Six grams (22.7 mmol) of 18-crown-6 crown ether were added to a 500 ml gas bulb filled with nitrogen. Glyme was distilled into the flask over nitrogen and a stir bar was added. Small pieces (each less than 0.05 g) of K (0.85 g, 21.7 mmol) were cut under mineral oil and added with a nitrogen blanket to the gas bulb. The solution turned blue and was evacuated to about 10 torr before being placed in liquid nitrogen. The gas bulb was evacuated and 17.6 mmol of SiH_4 were added. After warming to room temperature the solution was stirred for 5 h. To ensure an excess of SiH_4, the H_2 and SiH_4 were removed by vacuum and an additional 15.6 mmol of SiH_4 were condensed into the reaction bulb. The reaction was warmed to room temperature and was stirred for an additional 5 h until the potassium had disappeared and a white precipitate formed. The solvent was drawn off in a vacuum leaving a white powder, ($[K(18\text{-crown-6})]SiH_3$). Methylene chloride (0.96 g, 11 mmol) was condensed into the bulb at liquid nitrogen temperature. A reaction occurred as the temperature was raised to 15 °C over 30 min. The product gases were collected and analyzed to give $(H_3Si)_2CH_2$ (1.9 mmol; 17% yield), SiH_4 (5.25 mmol), H_3SiCH_3 (0.73 mmol), CH_2Cl_2 (0.85 mmol), and $ClCH_2SiH_3$ (0.14 mmol). A duplicate run using 35 ml of glyme gave the same products in similar amounts.

Results and discussion

Silane is the most direct starting compound for introducing the SiH_3 functional groups onto carbon compounds. Typically this is accomplished using a synthetic route proceeding through the SiH_3^- anion. The very slow rate of reaction between K and SiH_4 in polyether solvents has limited the exploitation of routes which use $KSiH_3$. We have found that addition of the appropriate crown ether increases the rate of reaction between SiH_4 and K in glyme by over a factor of one hundred to make this a synthetically useful route for generating the SiH_3^- anion. Although we did not isolate the anion, the reactions presented above are directly analogous to those reported for $KSiH_3$ without a crown ether and indicate the presence of the SiH_3^- anion [6,7].

The function of the crown ether is to complex K metal and its associated electron in solution where reactions with dissolved SiH_4 can occur. Our results are consistent with the following reaction pathway:

$$K_{solid} + 18\text{-crown-6} \rightarrow [K(18\text{-crown-6})]^+ + (e^-)_{solv} \qquad (5)$$

$$[K(18\text{-crown-6})]^+ + (e^-)_{solv} + SiH_4 \rightarrow [K(18\text{-crown-6})]SiH_3 + 0.5H_2 \qquad (6)$$

The bright blue color observed when K is added to glyme with 18-crown-6 in the absence of silane is indicative of "solvated electrons" [11]. As soon as SiH_4 is added, the blue color disappears as H_2 bubbles form and the "solvated electrons" are consumed.

We have not explored the use of crown ethers to enhance the reactivity of K/Na or K amalgams. It is likely that many of the routine reduction reactions that utilize alkali metals could be accelerated by the addition of crown ethers. We have not examined the effects of adding greater than stoichiometric amounts of crown ethers to further increase the rate of the reaction between K and SiH_4.

The characteristics of the reactions of various alkyl halides with [K(18-crown-6)]SiH_3 are the same as those reported for the uncomplexed $KSiH_3$ [6] with one significant difference. Previous investigators reported that the reaction of larger (gram) quantities of $KSiH_3$ with CH_2Cl_2 can result in detonations [12]. We observed only controlled reactions between organohalides and [K(18-crown-6)]SiH_3 run with or without solvent. Although we have not fully explored this point, it would be a synthetic advantage if one could decrease the danger of detonations by the use of [K(18-crown-6)]SiH_3 instead of $KSiH_3$.

It is not clear why the H_3SiCH_3 synthesis proceeded in reasonably good yield (64%) while the $(H_3Si)_2CH_2$ yield was much lower (17%). One plausible explanation is that some of the reaction product, $RSiH_3$, is consumed by the reactant [K(18-crown-6)]SiH_3 in an exchange with hydrogen atoms as shown in eq. 7, where R is an

$$SiH_3R + [K(18\text{-crown-6})]SiH_3 \rightarrow SiH_4 + [K(18\text{-crown-6})]SiH_2R \qquad (7)$$

alkyl or chloroalkyl group. In the specific case of H_3SiCH_3, $R = CH_3$, the desired product is a gas which can escape from the solution containing the reactant [K(18-crown-6)]SiH_3 before the exchange reaction, eq. 7, can occur to destroy the product. In the multi-stepped $(H_3Si)_2CH_2$ synthesis the less volatile product and intermediates could be subject to the above exchange reaction. If the exchange reaction is operative, the most likely way to maximize yields would be to run the reactions in such a way as to minimize contact between the reactants and products.

The proposed mechanism for product loss given in eq. 7 is supported by the large amounts of the by-product SiH_4 in the reactions. It is also well established from deuteration studies that the hydrogen atoms on SiH_4 and related compounds are labile [6], which is a prerequisite for the exchange mechanism.

We carried out the logical extension of our SiH_4 work to GeH_4. The reaction of GeH_4 with K and 18-crown-6 was examined in glyme as shown in eq. 8.

$$K + GeH_4 + 18\text{-crown-6} \rightarrow [K(18\text{-crown-6})]GeH_3 + 0.5H_2 \qquad (8)$$

The reaction to make [K(18-crown-6)]GeH_3 using a crown ether was analogous to that observed with silane except GeH_4 reacts even faster (within 30 min). The rate of reaction between K and GeH_4 in glyme, which is reasonably rapid, is increased further by a factor of about five by the addition of 18-crown-6.

Conclusions

We have demonstrated that adding crown ethers to K and SiH_4 reactions in polyether solvents reduces the synthesis time from months to hours to obtain SiH_3^- anions. The SiH_3^- anion is a versatile intermediate that can be used in a wide range of synthetic applications to introduce the SiH_3 functional group during the preparation of organosilicon compounds.

We have explored several of the synthetic pathways to $(H_3Si)_2CH_2$ and have identified the advantages of various routes to organosilane compounds. Use of [K(18-crown-6)]SiH_3 as a synthetic intermediate is excellent for rapidly obtaining smaller quantities, (one gram or less), of SiH_3 compounds in a single step. For preparation of more than gram quantities of $(H_3Si)_2CH_2$, the greater volumes of SiH_4 become more difficult to handle. We concur with other workers that multi-step syntheses through the intermediate $(Cl_3Si)_2CH_2$ are preferred for preparing larger quantities of $(H_3Si)_2CH_2$ [12,13].

Acknowledgements

We wish to thank Michael S. Milligan for analyzing some of the gas samples. We wish to acknowledge Dr. Dennis S. Rogers, UNISYS Corporation, for helpful suggestions and comments on early drafts of this paper.

This work was partially supported by the Solar Energy Research Institute (SERI) under Subcontract ZB-7-06003-2 to the Solarex Thin Film Division.

References

1 B.F. Fieselmann, M. Milligan, A. Wilczynski, J. Pickens, and C.R. Dickson, Conf. Record of 19th IEEE Photovoltaic Specialists Conf., IEEE, New York, 1987, p. 1510.
2 G. Fritz, J. Maas, and A. Hornung, Z. Anorg. Allg. Chem., 460 (1980) 115.
3 W.L. Jolly and A.D. Norman, Prep. Inorg. Reac., 4 (1968) 9.
4 G. Thirase and E. Weiss, Z. Naturforsch., 29b (1974) 800.
5 D.S. Rustad, T. Birchall, and W.L. Jolly, Inorg. Syn., 11 (1968) 128.
6 M.A. Ring and D.M. Ritter, J. Am. Chem. Soc., 83 (1961) 802.
7 E. Amberger, R. Romer, and A. Layer, J. Organomet. Chem., 12 (1968) 417.
8 S. Cradock, G.A. Gibbon, and C.H. van Dyke, Inorg. Chem., 6 (1967) 1751.
9 F. Feher, P. Plichta, and R. Guillery, Tetrahedron. Lett., (1970) 4443.
10 R. Varma and A.P. Cox, Angew. Chem. Internat. Ed. Engl., 4 (1964) 586.
11 J.L. Dye, Prog. Macrocyclic Chem., 1 (1979) 63.
12 J.A. Morrison and J.M. Bellama, J. Organomet. Chem., 92 (1975) 163.
13 R. Miller and G. Seitz, Chem. Ber., 91 (1958) 22.