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Activation of C-H Bonds of Heterocyclic and Alicyclic Compounds Using Calcium Atoms[1)]

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Synopsis. Calcium atoms have been inserted into C-H bonds of heterocyclic (furans and thiophene) and alicyclic compounds (cyclohexanes and cyclopentane) to give the corresponding organocalcium hydrides. The organocalcium hydrides thus produced reacted with trimethylchlorosilane to give trimethylsilyl-substituted heterocyclic and alicyclic compounds, and a reduced product (trimethylsilane).

The study of metal-vapor reactions is of considerable interest in organometallic chemistry and organic synthesis because by these methods, it is possible to synthesize organometallic compounds which would be difficult, if not impossible, to prepare by other methods, and to study their reactive intermediates.[2)]

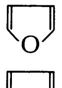
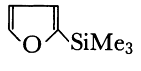
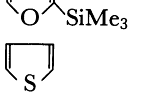
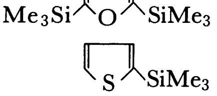
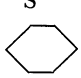
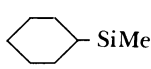
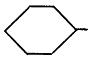
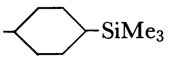
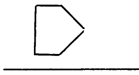
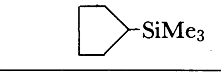
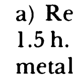
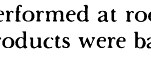
Activation of the C-H bond by metal atoms, clusters, and metal complexes is an area of intense research activity. In spite of this activation of the C-H bond by main group-metal atoms is still a rare phenomenon. Recently, we reported on the activation of the C-H bonds of substituted benzenes by calcium atoms.[3)] We have carried out the activation of the C-H bonds of heterocyclic and alicyclic compounds by calcium atoms.

In this paper, we describe the activation of the C-H bonds of heterocyclic and alicyclic compounds by calcium atoms.

Results and Discussion

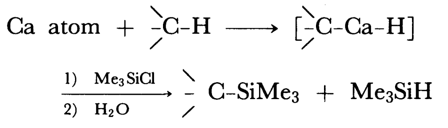
Calcium atoms were generated by evaporation from a tungsten filament using essentially the same apparatus and conditions as have been described in the literature (ca. 900 °C and 5×10^{-3} Torr, 1 Torr=133.322 Pa).[3-7)] Calcium metal was evaporated at a rate of ca. 20 mg min^{-1} while excess of the heterocyclic or alicyclic compound was co-condensed on the walls of the reaction flask containing the crucible and a perforated inlet tube through which the heterocyclic or alicyclic compound was admitted. The reaction flask was immersed in liquid nitrogen during the calcium evaporation. After the calcium evaporation and admission of the organic substrate was completed, the reaction flask was warmed to room temperature and the excess of trimethylchlorosilane was admitted as vapor and the reaction flask left to stand for 1.5 h. After removal of the reaction flask from a vacuum line, the reaction mixture was slowly hydrolyzed with water. The organic layer was extracted with ether.

Table 1. Reactions of Calcium Atoms/Heterocyclic and Alicyclic Compound Vapors with Trimethylchlorosilane[a)]

Substrate	Products	(Yield/%[b)])	
		(3.0)	Me_3SiH (1.0)
		(4.0)	Me_3SiH (4.0)
		(1.0)	Me_3SiH (1.0)
		(1.0)	Me_3SiH (1.0)
		(1.0)	Me_3SiH (1.0)
		(1.0)	Me_3SiH (1.0)

a) Reactions were performed at room temperature for 1.5 h. b) Yields of products were based on the calcium metal consumed.

Hydrolysis of the products gave trimethylsilyl-substituted products, and a reduced product (trimethylsilane) (Eq. 1). All products were identified by comparing their GC-MASS and retention times on GLC with those of authentic samples. The results are summarized in Table 1.



$$\text{Ca atom} + \rangle\text{C-H} \longrightarrow [\rangle\text{C-Ca-H}] \xrightarrow[2)\ H_2O]{1)\ Me_3SiCl} \rangle\text{C-SiMe}_3 + \text{Me}_3\text{SiH} \qquad (1)$$

As shown in Table 1, the reaction products of calcium atoms/furan, 2-trimethylsilylfuran, and thiophene vapors when treated with trimethylchlorosilane gave 2-trimethylsilylfuran, 2,5-bis(trimethylsilyl)furan, and 2-trimethylsilylthiophene, respectively, and trimethylsilane in very low yields. No 3-trimethylsilylfuran, 2,3-, 2,4-bis(trimethylsilyl)furan, and 3-trimethylsilylthiophene were produced. A theoretical calculation for anion radicals of five-membered ring compounds has been made.[8)] It appears that the position of calcium atom attack may be influenced by the unpaired spin density. Accordingly we suggest that the reaction sequence may be (1) electron transfer to form a Ca^+ five-membered ring compound$^{\cdot-}$, and (2) attack of the Ca^+ at the most electron-rich site. Thus selective insertion of calcium atoms into C-H bonds may depend upon the spin densities of the heterocyclic compound anion radicals.

The reaction products of calcium atoms/cyclohexane, methylcyclohexane, and cyclopentane vapors when treated with trimethylchlorosilane gave cyclohexyltrimethylsilane, 4-methylcyclohexyltrimethylsilane, and cyclopentyltrimethylsilane, respectively, and trimethylsilane in very low yields as shown in Table 1. The insertion mechanism of C-H bonds of alicyclic compounds with calcium atoms is not clear. It is not possible to predict whether electron transfer occurs between calcium atoms and the alicyclic compound in the vapor state.

Although the yields of products are very low as shown in Table 1, this is a first example of ^{sp3}C-H bond activation with calcium metal.

Calcium hydride is known to be incapable of reducing trimethylchlorosilane. However, the organic calcium hydride thus prepared can reduce trimethylchlorosilane to give trimethylsilane.

The yields of trimethylsilyl-substituted products and reduced product (trimethylsilane) as shown in Table 1 are very low. The yields of these products were determined on the basis of the amount of calcium metal consumed on the assumption that all of the vaporized calcium metal reacted completely with the heterocyclic and alicyclic compound vapors. Therefore, taking into consideration that the calcium insertion products include a large amount of unreacted calcium metal, the yields of the products as shown in Table 1 may be considerably underestimated.

The co-condensation product which was formed by deposition of calcium atoms onto the frozen layer of heterocyclic and alicyclic compound or by condensation of the organic substrate vapor onto the layer of calcium atoms did not react with trimethylchlorosilane under these reaction conditions.

Experimental

GLC analyses were performed on a Shimazu GC-6A and 8A gas chromatograph with 2m 20% SE-30 and 2m 30% Apiezon L columns. GC-MASS spectra were obtained with JEOL JMS-DX 303 mass spectrometer. NMR spectra were obtained with a Varian FT-80A spectrometer using $CDCl_3$ as the solvent and TMS as the internal standard.

Materials. Calcium metal (granule, 99% pure, Wako chemicals) was commercially available. Furan, thiophene, cyclohexane, methylcyclohexane, and cyclopentane were dried and distilled prior to use. 2-Trimethylsilylfuran,[9] 2,5-bis(trimethylsilyl)furan,[10] 2-trimethylsilylthiophene,[9] cyclohexyltrimethylsilane,[11] 4-methylcyclohexyltrimethylsilane,[12] and cyclopentyltrimethylsilane[13] were prepared as described in the references cited.

Reactions of Calcium Atoms/Heterocyclic and Alicyclic Compound Vapors with Trimethylchlorosilane. As a typical example, the reaction of calcium atoms/furan vapor with trimethylchlorosilane is described. Calcium metal (200 mg, 5.0 mmol) was vaporized at a temperature of ca. 900 °C using a filament of tungsten in vacuo (ca. 5×10^{-3} Torr) at a rate of ca. 20 mg min^{-1}. During the vaporization of calcium metal, furan (20 cm^3, 276 mmol) was introduced into the reaction vessel as vapor. Calcium atoms/furan vapor condensed on the wall of the reaction vessel which was cooled to 77 K with liquid nitrogen. The initial product at 77 K was a muddy yellow. The reaction vessel was warmed to room temperature and trimethylchlorosilane (15 cm^3, 118 mmol) was then admitted as vapor. The reaction vessel was left to stand for 1.5 h. After removal of the reaction vessel from a vacuum line, the reaction mixture was slowly hydrolyzed with water. The organic layer was extracted with ether. The products were identified by comparing their GC-MASS and retention times on GLC with those of authentic samples. The yields of the products were determined by an internal-standard method.

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References

1) Y. Yoshida, T. Yamanishi, and K. Mochida, 52nd National Meeting of the Chemical Society of Japan, Kyoto, April 1986, 1K29.

2) For examples; J. R. Blackborow, "Metal Vapor Synthesis in Organometallic Chemistry," Springer-Verlag, New York (1979); K. J. Klabunde, "Chemistry of Free Atoms and Particles," Academic Press, New York (1980); K. J. Klabunde, "Reactive Intermediates," ed by R. A. Abramovitch, Plenum Press, New York (1980), Chapt. 2; R. H. Crebtree, *Chem. Rev.*, **85**, 245 (1985).

3) K. Mochida, H. Takeuchi, Y. Hiraga, and H. Ogawa, *Chem. Lett.*, **1984**, 1989.

4) K. Mochida and H. Ogawa, *J. Organomet. Chem.*, **243**, 131 (1983).

5) K. Mochida and M. Manishi, *Chem. Lett.*, **1984**, 1077.

6) K. Mochida and Y. Mizuno, *Chem. Lett.*, **1986**, 1125.

7) K. Mochida and Y. Mizuno, *Bull. Chem. Soc. Jpn.*, **60**, 273 (1987).

8) M. M. Urberg and E. T. Kaiser, "Radical Ions," ed by E. T. Kaiser and L. Kevan, Interscience, New York (1968), Chapt. 8.

9) R. A. Benkeser and R. B. Currie, *J. Am. Chem. Soc.*, **70**, 1780 (1948).

10) C. S. Carman and G. F. Koser, *J. Org. Chem.*, **48**, 2534 (1983).

11) N. S. Nametkin, A. V. Topchiev, and T. I. Chernysheva, *Dokl. Akad. Nauk SSSR*, **110**, 97 (1956).

12) J. C. Saam and J. L. Speier, *J. Am. Chem. Soc.*, **83**, 1351 (1961).

13) G. A. Russell and K. L. Nagpal, *Tetrahedron Lett.*, **1961**, 421.