SHORT COMMUNICATIONS

Aluminum Chloride-Catalyzed Reactions of Organosilicon Compounds. A Rapid Redistribution Reaction of Chlorodisilanes

By Hideki SAKURAI, Kenji TOMINAGA and Makoto KUMADA

Department of Synthetic Chemistry, Kyoto University, Sakyo-ku, Kyoto

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In recent years, considerable attention has been directed toward a study of the organopolysilanes.¹⁾ An interesting example of this involves the reaction of organodisilanes with an electrophilic reagent.²⁾ During the course of an investigation of the reactivity of organopolysilanes toward electrophiles, we have found that methylchlorodisilanes readily undergo aluminum chloride-catalyzed redistribution reaction at room temperature, while the disproportionation of alkylchlorosilanes catalyzed by aluminum chloride has been reported to proceed slowly, even at much higher temperatures.^{3,4)}

 $(CH_{3})_{3}SiSi(CH_{3})_{3} + Cl(CH_{3})_{2}SiSi(CH_{3})_{2}Cl$ $\xrightarrow{AlCl_{3}}{\longleftarrow} 2(CH_{3})_{3}SiSi(CH_{3})_{2}Cl \qquad (1)$

When an equimolar mixture of hexamethyldisilane and 1, 2-dichlorotetramethyldisilane is stirred at room temperature in the presence of anhydrous aluminum chloride (0.05-0.25 mol./1.), the equilibrium is established between pentamethylchlorodisilane and its original components within 1.5 hr.⁵

As the equilibrium is established rapidly in favor of pentamethylchlorodisilane, the reaction can be applied in a preparative scale. In a typical experiment a mixture of 73.5 g. of hexamethyldisilane, 94.5 g. of tetramethyldichlorodisilane, and 5.5 g. of anhydrous aluminum chloride was stirred for about 2 hr. at room temperature. After 3 g. of acetone had been added to the mixture to deactivate the catalyst, the mixture was subjected to simple distillation under reduced pressure. The fractionation of the distillate gave 114 g. (68.5%) of pure pentamethylchlorodisilane.

In view of these finidings, it became of interest to investigate the aromatic substitution by a mixture of pentamethylchlorodisilane and aluminum chloride, since it is well known that halosilanes do not react with benzene in the presence of Lewis $acid.^{3,4)}$

Although an attempted silvlation of benzene by a mixture of pentamethylchlorodisilane and aluminum chloride was unsuccessful, we have found that detrimethylsilvlation was effected very rapidly by pentamethylchlorodisilane in the presence of a catalytic amount of aluminum chloride.

$$C_{6}H_{5}Si(CH_{3})_{3} + Cl-Si(CH_{3})_{2}Si(CH_{3})_{3} \xrightarrow{AiCl_{3}} C_{6}H_{5}Si(CH_{3})_{2}Si(CH_{3})_{3} + Cl-Si(CH_{3})_{3}$$
(2)

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Using competitive reaction conditions in benzene, we found that phenyltrimethylsilane underwent the reaction faster than p-chlorophenyltrimethylsilane and slower than p-methylphenyltrimethylsilane with pentamethylchlorodisilane.⁶

The order of substituent effects demonstrates the electrophilic nature of the reaction; it also confirms the present reaction to be a new class of aromatic electrophilic substitution.⁷

¹⁾ C. Eaborn, "Organosilicon Compounds," Butterworths Scientific Publications, London (1960), p. 351.

²⁾ H. Sakurai, T. Imoto, N. Hayashi and M. Kumada, J. Am. Chem. Soc., 87, 4001 (1965). 3) H. Gilman and G. E. Dunn, Chem. Revs., 52,

³⁾ H. Gilman and G. E. Dunn, *Chem. Revs.*, 52, 77 (1953).

⁴⁾ G. A. Russell, J. Am. Chem. Soc., 81, 4831 (1959), and references therein.

⁵⁾ The apparent equilibrium constant, $K=[C_5H_{15}-Si_2Cl]^2/[C_6H_{18}Si_2][C_4H_{12}Si_2Cl_2]$, was found to be 82.6 for the original mixture of 6.22 mmol. of hexamethyldisilane, 5.78 mmol. of tetramethyldichlorodisilane and 1 mmol. of aluminum chloride in 20 ml. of benzene. In chloroform, however, the reaction did not proceed even after one week at room temperature.

⁶⁾ The apparent relative rates at an early stage of the reaction were found: $k_{p-CH_3}/k_{\rm H}=2.0$ and $k_{p-Cl}/k_{\rm H}=0.2$.

 $k_{\rm H}=0.2$. 7) R. O. C. Norman and R. Taylor, "Electrophilic Substitution in Benzenoid Compounds," Elsevier Pubshing Co., Amsterdam (1965).