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# ALUMINUM CHLORIDE-CATALYZED REACTIONS OF ORGANOSILICON COMPOUNDS II. FACILE SYNTHESES OF ALKYLCHLOROSILANES, -GERMANES, AND -STANNANES (1)

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During the course of an investigation of the reactivity of organopolysilanes toward electrophiles (2), we have found that methylchlorodisilanes undergo an aluminum chloride-catalyzed redistribution reaction readily at room temperature (1), while the disproportionation of alkylchlorosilanes catalyzed by aluminum chloride was reported to proceed slowly even at much higher temperatures (3,4).

$$(CH_3)_3SiSi(CH_3)_3 \ + \ Cl(CH_3)_2SiSi(CH_3)_2Cl \ \overset{AlCl_3}{\rightleftharpoons} \ Cl(CH_3)_2SiSi(CH_3)_3$$

As an extension of these findings, we have studied on the interactions of organosilicon compounds with RCl, where R= $(CH_3)_3SiSi(CH_3)_2$, H, alkyl, benzoyl and acetyl, and found that these reactions generally lead to the formation of the corresponding alkylchlorosilanes in good yield. Especially the reactions of methylpolysilanes or carbosilanes with dry hydrogen chloride or acetyl chloride in the presence of anhydrous aluminum chloride are of great value in the synthesis of the corresponding methylchlorosilanes. Thus, hexamethyldisilane reacts exothermally with bubbling dry hydrogen chloride at room temperature in the presence of a catalytic amount of aluminum chloride to yield pentamethylchlorodisilane. As shown in Table 1 dichlorotetramethyldisilane as well as trichlorotrimethyldisilane were also prepared in satisfactory yields from hexamethyldisilane by controlling the reaction temperature. The end point of the reaction can be measured by g.l.c., after deactivation of the catalyst to prevent undesirable redistribution (1) before isolation of the products (5).

Dealkylation of alkylsilanes with acetyl chloride and aluminum chloride affords another convenient and widely applicable method of the preparation of chlorosilanes. In a typical experiment 35 g (0.45 mole) of acetyl chloride was added dropwise to a slurry of 40 g (0.20 mole) of octamethyltrisilane and 53 g (0.40 mole) of aluminum chloride with stirring. A moderate exothermic reaction took place and finally the mixture became homogeneous. After the addition was completed the mixture was stirred for 2 hr. The product was simply removed from the mixture by distillation under a reduced pressure. After fractionation through a 25 cm column packed with glass helicoils, 1,3-dichlorohexamethyltrisilane (40 g, 84 %) was obtained as a colorless, pure liquid. Following

## TABLE 1

PREPARATION OF SOME ALKYLCHLOROSILANES, -STANNANES AND -GERMANES.

| Starting Compound | Method | Temp. | Product | Yield (%)[f] |
|---|---|---|---|---|
| $(CH_3)_3SiSi(CH_3)_3$ | A[a] | e | $(CH_3)_3SiSi(CH_3)_2Cl$ | 73 |
| $(CH_3)_3SiSi(CH_3)_3$ | A | 50-60° | $Cl(CH_3)_2SiSi(CH_3)_2Cl$ | 81 |
| $(CH_3)_3SiSi(CH_3)_3$ | A | 90° | $Cl(CH_3)_2SiSi(CH_3)Cl_2$ | 70 |
| $(CH_3)_4Si$ | B[b] | e | $(CH_3)_3SiCl$ | 97[g] |
| $(C_2H_5)_4Si$ | B'[c] | e | $(C_2H_5)_2SiCl_2$ | 92[g] |
| $(CH_3)_3SiSi(CH_3)_3$ | B | e | $(CH_3)_3SiSi(CH_3)_2Cl$ | 85 |
| $(CH_3)_3SiSi(CH_3)_3$ | B' | e | $Cl(CH_3)_2SiSi(CH_3)_2Cl$ | 87 |
| $(CH_3)_3SiSi(CH_3)_3$ | B"[d] | ~125° | $Cl(CH_3)_2SiSi(CH_3)Cl_2$ | 74 |
| $(CH_3)_3SiSi(CH_3)_2Si(CH_3)_3$ | B | e | $(CH_3)_3SiSi(CH_3)_2Si-(CH_3)_2Cl$ | 66 |
| $(CH_3)_3SiSi(CH_3)_2Si(CH_3)_3$ | B' | e | $Cl(CH_3)_2SiSi(CH_3)_2Si-(CH_3)_2Cl$ | 84 |
| $[(CH_3)_3Si]_2CH_2$ | B' | e | $[Cl(CH_3)_2Si]_2CH_2$ | 70 |
| $[(CH_3)_3Si]_3CH$ | B" | e | $[Cl(CH_3)_2Si]_3CH$ | 87 |
| $(CH_3)_3SiCH_2CH_2Si(CH_3)_3$ | B' | e | $Cl(CH_3)_2SiCH_2CH_2Si-(CH_3)_2Cl$ | 95 |
| $(CH_3)_4Sn$ | B | e | $(CH_3)_3SnCl$ | 70 |
| $(CH_3)_4Sn$ | B' | e | $(CH_3)_2SnCl_2$ | 90[g] |
| $(CH_3)_4Ge$ | B | e | $(CH_3)_3GeCl$ | 74 |
| $(CH_3)_4Ge$ | B' | e | $(CH_3)_2GeCl_2$ | 70 |

[a] The reaction with dry hydrogen chloride in the presence of

catalytic amount (~5 %) of anhydrous aluminum chloride. [b] The reaction with acetyl chloride and anhydrous aluminum chloride, the amount of each reagent being equivalent to the starting compound. [c] Starting Compound/$CH_3COCl/AlCl_3$ = 1:2:2. [d] Silane/$CH_3COCl/AlCl_3$ = 1:3:3. [e] Maintained at about room temperature with moderate external cooling. [f] Unless otherwise stated, yields are based on the amount of the product obtained after fractional distillation through a 25 cm column packed with glass helicoils. [g] Yields after simple distillation.

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this general procedure, a wide variety of other alkylchlorosilanes were prepared in good yield and some of the results are listed in Table 1.

The reaction was also applicable to the preparation of alkylchlorostannanes and germanes. Trimethylchlorostannane and dimethyldichlorostannane were prepared from tetramethylstannane in 70 and 90 % yield, respectively. Similarly, trimethylchlorogermane and dimethyldichlorogermane were prepared from tetramethylgermane in 74 and 70 % yield, respectively.

The later method for the direct chlorodealkylation of alkylsilanes, -germanes and -stannanes constitutes a preferred, one step procedure for synthesis of the corresponding alkylchloro compounds in certain cases.

Acceptable C, H, and Cl analyses were obtained for all the products in Table 1. Their structures were unequivocally established through nmr and ir spectroscopic studies and through comparison of their physical properties with those of authentic samples. Details will be published elsewhere soon later.

## REFERENCES

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(5) We have examined several compounds as deactivating reagents for aluminum chloride and found that acetone may be most useful.