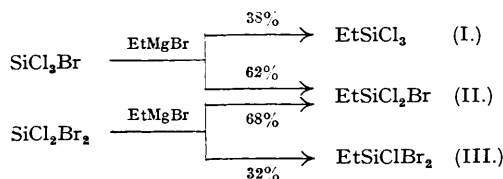


34. *Experiments on the Substitution Behaviour of the Silicon Chlorobromides.*

By C. J. WILKINS, N. P. H. BROWN, and ALISON D. STEVENS.

Trichlorobromosilane and dichlorodibromosilane react with Grignard reagents with replacement of both chlorine and bromine, the proportion of bromine replaced being higher the larger the alkyl group. From the reactions of these silicon chlorobromides with ethylmagnesium bromide ethyldichlorobromosilane and ethylchlorodibromosilane have been isolated. Chlorotribromosilane and tetrabromosilane are unreactive towards Grignard reagents.

ALTHOUGH silicon tetrachloride reacts readily with alkylmagnesium bromides, experiments made in this laboratory by Lorking have shown that this reactivity does not extend to the tetrabromide, which indeed, fails to yield substitution products with methylmagnesium bromide at temperatures below 160°. Our results on the behaviour of the silicon chlorobromides towards Grignard reagents have shown that chlorotribromosilane resembles tetrabromosilane (silicon tetrabromide) in being unreactive; trichlorobromosilane and dichlorodibromosilane do, however, react. Both halogens undergo replacement, and with ethylmagnesium bromide the reactions proceed thus :



The percentages represent the atomic ratio of the two halogens from the silicon chlorobromide found in the precipitated magnesium halide from preparative experiments. Yields of the purified products (I), (II), and (III) were in similar proportions. The compounds, *ethyldichlorobromosilane* (II), b. p. 120—121°/768 mm., and *ethylchlorodibromosilane* (III), b. p. 141—143°/768 mm., are the first organo-substituted silicon chlorobromides to be reported. It has not proved possible to obtain the corresponding methyl compounds in a state of purity owing, it seems, to the proximities of the boiling points of the reactants and products.

In the series of tetrahalides examined the effect of the accumulation of bromine in reducing the reactivity not only of the bromine atoms themselves, but also of the adjacent chlorine, may well be connected with the steric influence of the rather large bromine atoms. Evidence for this view was obtained from an examination of the relative proportions of chlorine and bromine replaced from trichlorobromosilane and dichlorodibromosilane on their reaction with a series of Grignard reagents containing successively larger alkyl groups. It will be noticed from the following table that the larger the attacking group the higher the proportion of the larger halogen replaced.

| Reagent. | MeMgBr. | EtMgBr. | Pr ^t MgBr. | Bu ^t MgCl. |
|---|---------|---------|-----------------------|-----------------------|
| Halide from SiCl ₃ Br, Cl, %..... | — | 60 | 44 | 0 |
| „ „ Br, % | — | 40 | 56 | 100 |
| „ SiCl ₂ Br ₂ , Cl, % | 52 | 39 | 5 | — |
| „ „ Br, % | 48 | 61 | 95 | — |

These results, from experiments carried out on a small scale (0.01—0.02 g.-mol.) under comparable conditions, were again obtained by analysis of the precipitated magnesium halide. No attempt was made to isolate the volatile products from this series of reactions. Whilst high reproducibility could not be expected, the compositions of magnesium halide from the small-scale and preparative experiments using ethylmagnesium bromide are in reasonable accord.

EXPERIMENTAL.

Preparation of Silicon Chlorobromides.—Each of these three compounds was obtained from the reaction of silicon tetrabromide with the theoretical quantity of antimony trichloride (Schumb and Anderson, *J. Amer. Chem. Soc.*, 1937, **59**, 651). A mild reaction occurred on heating the mixture, and the product was tapped off at the appropriate temperature from the head of a 14-in. (Whitmore and Lux type) fractionating column packed with Fenske helices. After re-fractionation of the product yields were about 70%.

Silicon tetrabromide itself was obtained by passing bromine vapour over powdered silicon in a silica tube heated to redness. The product was left over mercury to remove free bromine, and distilled.

Reactions with Grignard Reagents.—In experiments conducted on a preparative scale the general

procedure introduced by Kipping was followed. The reaction was carried out in an ice-cooled flask fitted with dropping funnel, stirrer, and reflux condenser. A solution of the Grignard reagent in ether was run slowly, with stirring, into the silicon chlorobromide diluted with 2—3 times its volume of ether. With trichlorobromosilane there was an immediate separation of magnesium halide, but dichlorodibromosilane was less reactive and the halide precipitate appeared only on heating the mixture under reflux. The magnesium halide was filtered off and extracted with ether, and the liquid fractionally distilled to remove ether and separate alkylated products.

In the reactions carried out on a small scale to establish the course of the substitution, equimolecular quantities of the reactants were heated under reflux until no more magnesium halide separated. The solution was then poured off, and the halide washed with hot ether and dissolved in water for analysis.

Analysis.—Chloride and bromide in admixture were determined by precipitation as silver halide, and a Mohr titration. In some instances bromide figures were checked by titration (in a separating funnel) with freshly standardised chlorine water, the titration being continued until the colour of bromine just failed to appear in successive small quantities of chloroform used as extractant. The silicon content of a compound was determined by hydrolysis in a platinum crucible containing water, followed by evaporation and ignition.

In certain cases determination of the strong acid liberated on hydrolysis sufficed to identify a compound.

The Products from Trichlorobromosilane and Ethylmagnesium Bromide.—The Grignard reagent (0.25 g.-mol.) was added to trichlorobromosilane (0.25 g.-mol.), and stirring was continued for half an hour whilst the mixture warmed to room temperature. Magnesium halide was removed and the ether distilled off. The residual liquid (about 30 c.c.) was decanted from a further small precipitate of magnesium halide, and carefully fractionated in an all-glass apparatus using the column mentioned above. The first distillation indicated the presence of components boiling in the vicinity of 80°, 100°, and 120°. Three systematic redistillations yielded about 1 c.c. of unreacted trichlorobromosilane (b. p. 80—82°), 5 c.c. of ethyltrichlorosilane (b. p. 99—102°), and 10 c.c. of *ethyl*dichlorobromosilane (b. p. 120—121°) together with incompletely resolved intermediate fractions (Found, fraction b. p. 99—102°: Cl, 63.8; Br, 1.7%. Calc. for EtSiCl_3 : Cl, 65.6%. Found, fraction b. p. 120—121°: Cl, 33.9; Br, 37.5; Si, 13.9%. EtSiCl_2Br requires Cl, 34.1; Br, 38.4; Si, 13.5%).

The Products from Dichlorodibromosilane and Ethylmagnesium Bromide.—When equivalent quantities (0.4 g.-mol.) of the two reactants were mixed no reaction occurred in the cold, the Grignard reagent forming an oily lower layer. Magnesium halide separated during five hours' heating of the mixture under reflux, after which the products were isolated as before. There were obtained about 1 c.c. of unreacted dichlorodibromosilane (b. p. 105—107°), 14 c.c. of ethyldichlorobromosilane (b. p. 119.5—122°), and 4 c.c. of *ethyl*chlorodibromosilane (b. p. 141—143°) (Found, fraction b. p. 119.5—122°: 0.0141 equiv. of acid per g. Calc. for EtSiCl_2Br : 0.0144. Found, fraction b. p. 141—143°: Cl, 13.8; Br, 61.4; Si, 11.3%. EtSiClBr_2 requires Cl, 14.1; Br, 63.3; Si, 11.1%.) It is suspected that the low figure for bromine in the analysis of the second ethyl compound may be due to slight further substitution of this halogen to give an impurity having similar volatility.

Attempted Methylation of Chlorotribromosilane.—The chlorobromide was heated under reflux for several hours with an ethereal solution of methylmagnesium bromide, but magnesium halide did not separate and two liquid layers remained. Next, the silicon halide and the solid Grignard reagent (0.33 g.-mol. of each) were heated at 120° for 10 hours; the recovered liquid, distilling at 125—135°, was essentially unreacted chlorotribromosilane (Found: 0.0134 equiv. of acid per g. Calc. for SiClBr_3 : 0.0132; for MeSiBr_3 , 0.0106; for MeSiClBr_2 , 0.0126).

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CANTERBURY UNIVERSITY COLLEGE,
CHRISTCHURCH, NEW ZEALAND.

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