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NOTE

FRIEDEL–CRAFTS REACTIONS OF SILICON HALIDES

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It is generally accepted that silicon halides unlike organic halides do not undergo Friedel–Crafts reactions[1]. An apparent exception is the reported reaction of silicon tetrachloride with olefins and acetylene under mild conditions when catalyzed by large quantities of aluminum chloride or similar reagents. Thus Shtetter has disclosed the following reactions taking place at room temperature and under normal pressure[2]. These would appear to parallel the reaction of tert-butyl chloride with ethylene[3].

$$SiCl_4 + CH_2{=}CH_2 \rightarrow Cl_3SiCH_2CH_2Cl$$

$$SiCl_4 + HC{\equiv}CH \rightarrow Cl_3SiCH{=}CHCl$$

$$(CH_3)_3CCl + CH_2{=}CH_2 \xrightarrow{AlCl_3} (CH_3)_3CCH_2CH_2Cl$$

Although the reactions have been cited in standard textbooks on organosilicon chemistry[4,5] doubts have remained as no subsequent publications have appeared. Because of other interests in Friedel–Crafts reactions[6], we have now attempted to confirm these reactions.

EXPERIMENTAL

Shtetter's experimental details are limited to a single example for the reaction of silicon tetrachloride with ethylene[2]. We have repeated the reaction conditions closely with some changes in work-up to permit improved material balance and product identification. Shtetter treated his reaction mixture with hydrochloric acid to separate the product from the catalyst. The product was then obtained in polymeric form as (2-chloroethyl)siloxane. We have substituted solvent extraction for this step in order to obtain more readily identifiable monomeric products.

Reaction of silicon tetrachloride with ethylene

Into a 300-ml stainless steel autoclave fitted with a pressure head, gage and gas inlet port was charged 50 g (0.295 mole) $SiCl_4$ (>98 % pure by VPC), 50 g (0.375 mole) anhydrous purified $AlCl_3$ powder (Matheson, Coleman and Bell) and 4 g red HgO (Fisher Certified Grade). The autoclave was pressured with 150 psi of nitrogen and then pressured to 375 psi with ethylene (Matheson research grade, 99.5 %) at 20°.

Ethylene was taken up as the autoclave was rocked and the vessel was repressured to 375 psi as needed. A total pressure drop of 700 psi (approximately 0.5 mole) was observed after 2 h. Pressuring with ethylene was discontinued in order to follow Shtetter's conditions. Although Shtetter indicates[2] that only one mole ethylene reacts per mole of $SiCl_4$, our observations would indicate that reaction continues well past this point. The pressure vessel was vented and slurried with 300 ml pentane to collect the products. Low-boiling products were isolated by vacuum stripping at 25°/0.5 mm. Titration of the volatiles (340 ml) indicated 0.286 mole (97 % recovery) of $SiCl_4$. This was confirmed by VPC by comparison with authentic $SiCl_4$ in pentane.

The solid residue (71.7 g) was extracted several times with pentane. Upon filtration 60 g of solids were recovered. Analysis of the solids indicated < 0.02 % Si. Pentane was removed by atmospheric distillation through a 12 in. Vigreaux column leaving 11 g of a clear viscous oil. [Found: C, 85.4; H, 14.6. $(C_2H_4)_n$ calcd.: C, 85.7; H, 14.3 %; no Si or Cl.] IR confirmed hydrocarbon composition. Expected bands for C–H stretching, deformation, $(CH_2)_n$ and (CH_3) are all present. NMR confirmed hydrocarbon structure as a highly branched polyethylene.

Reaction of silicon tetrachloride with acetylene

Into a 200-ml 2-neck flask fitted with a thermometer and condenser was placed 50 g $SiCl_4$, 25 g $AlCl_3$ and 2 g red HgO. The mixture was stirred at 25° under nitrogen as acetylene (Matheson) which was first passed through activated silica gel was bubbled through the stirred slurry at the rate of 0.5 l/min for 3 h. No exotherm was noted. Vacuum stripping recovered 20 g $SiCl_4$ (99 % pure by VPC). The unrecovered $SiCl_4$ was sparged from the system by the flow of acetylene. No higher-boiling components were detected by VPC. The solid residue (27.5 g) showed a net increase of 0.5 g. Extraction of the salt mass several times with warm pentane did not yield any volatile products detectible by VPC. Removal of the pentane by distillation left approximately 0.2 g of a clear oil. IR indicated that the oil was a mixture of branched hydrocarbons and a polydimethylsiloxane (probably extracted from the greased glass joints). Analysis of the salt residue, Si, 0.03 %.

Vapor phase chromatography

Data was obtained on an F and M 700 Gas Chromatograph using a 4' stainless steel column 1/4" OD packed with 20 % of SE-30 silicone rubber on a substrate of 60 × 80 Chromosorb W and a helium carrier gas rate of 50 cc/min. Injection port temperature was 250°, detector temperature 320° and filament current 150 mA. One and one half microliters of sample was usually injected, starting at 40° and programming at 5°/min.

RESULTS AND DISCUSSION

It is evident that reaction does not occur between silicon tetrachloride and ethylene or acetylene to give the adducts claimed by Shtetter. Instead the olefin is polymerized to a low molecular weight hydrocarbon free of silicon substitution. Shtetter claimed that (2-chloroethyl)trichlorosilane complexed with the catalyst and had to be isolated by treatment with hydrochloric acid. We have found no evidence for the formation of (2-chloroethyl)trichlorosilane either free or complexed. It is possible that treatment with hydrochloric acid yielded a mixture of hydrocarbon oil and chlorine-containing silica (arising from $SiCl_4$) to account for the results reported.

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