Journal of Organometallic Chemistry, 59 (1973) 141–144

THE METHANOLYSIS AND HYDROGENOLYSIS OF SOME ALKOXYSILANES

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(Received January 19th, 1973)

SUMMARY

A number of alkoxysilanes have been prepared and investigations carried out on their stability, methanolysis and hydrogenolysis. Hydrogen at atmospheric pressure and room temperature over a palladium on charcoal catalyst cleaves many alkoxysilanes to give a hydrocarbon plus siloxane.

INTRODUCTION

The initial aim of this work was a search for protective groups for silanols to assist in our investigations on the separation and study of stereoisomeric organosilicon compounds. We commenced by studying the preparation of trityl and benzyl derivatives since alcohol groups are often protected by the formation of such derivatives, particularly in carbohydrate chemistry, and the protecting group can subsequently be removed by hydrogenolysis. Difficulties were encountered in the preparation of trityl derivatives of silanols, but the benzyl and other derivatives were the object of a series of observations on stability, methanolysis and hydrogenolysis which we report here.

The compounds used in this work were all prepared by reaction of the appropriate chlorosilane and alcohol in ether solution with pyridine as acid acceptor. The products of reaction could all be distilled without decomposition and although apparently quite stable when kept in a dry inert atmosphere some of them were susceptible to attack by atmospheric moisture and oxygen upon prolonged storage. For example (benzyloxy)trimethylsilane underwent extensive decomposition on keeping for twelve months in a stoppered flask. IR spectroscopy indicated that the products were benzoic acid, benzaldehyde, benzyl alcohol and hexamethyldisiloxane. This decomposition appears to be a combined process of hydrolysis and oxidation by

$$2\ PhCH_2OSiMe_3 + H_2O \rightarrow PhCHO + PhCH_2OH + Me_3SiOSiMe_3 \qquad (1)$$

atmospheric moisture and oxygen, since a sample sealed under vacuum showed no signs of decomposition after eighteen months. It has been reported[1] that (benzyloxy)triethylsilane decomposes on long standing in air to give dibenzyl ether and hexaethyldisiloxane.

In the alcoholysis of esters attack may occur either at the carbonyl carbon atom or at the carbon–oxygen bond, according to the nature of the ester. In the cleavage of alkoxysilanes by alcohols attack is normally at the silicon atom, as would be expected. It was of interest to see whether this was still the case when the alkoxysilane contained an aralkyl group which would readily form a carbonium ion. In the compounds which we investigated the only products observed were those which would be expected from attack at silicon, according to eqn. (2).

$$Me_3SiOR + CH_3OH \rightleftarrows Me_3SiOCH_3 + ROH \qquad (2)$$

With a group of compounds in which R contained aromatic residues both the position and rate of attainment of equilibrium varied with the nature of R, and were in the order $C_6H_5CH_2$, $(C_6H_5)_2CH$, $CH_3(C_6H_5)CH$, $(CH_3)_2C_6H_5C$. Compounds containing groups earlier in this series react faster and the equilibrium lies further to the right.

Several catalytic hydrogenations of alkoxysilanes have been previously reported. Thus *o*-tolyltriethoxysilane was reduced to (2-methylcyclohexyl)triethoxysilane[2] and [4-(trimethylsilyl)phenoxy]trimethylsilane was reduced[3] to [4-trimethylsilyl)cyclohexyloxy]trimethylsilane. In these cases the hydrogenation was carried out under pressure, at a temperature of 95–105° and over a Raney-nickel catalyst. With a ruthenium-on-charcoal catalyst at 125° and a pressure of 170 atm. the aromatic rings in 1-naphthylphenylmethyl-(−)-menthoxysilane were completely hydrogenated[4]. In these reactions the Si–O–C bonds remained intact during the reaction. On the other hand hydrogenation of a number of trialkylalkoxysilanes over nickel catalysts at high pressures and temperatures is reported[5] to result in the cleavage of the Si–O–C bonds with the formation of hydrocarbons, disiloxanes and silanols. With hydrogen at atmospheric pressure and room temperature over a palladium-on-charcoal catalyst we have found that many alkoxysilanes are smoothly cleaved to give a hydrocarbon plus siloxane. Thus (benzyloxy)trimethylsilane dissolved in cyclohexane reacts over a period of 20 min to give almost quantitative yields of toluene and hexamethyldisiloxane. The reaction can readily be followed from the hydrogen uptake and the reaction products identified by GLC. Similarly (diphenylmethoxy)trimethylsilane, (α, α-dimethylbenzyloxy)trimethylsilane and (α-methylbenzyloxy)trimethylsilane all gave hexamethyldisiloxane and the corresponding hydrocarbons. In the initial stages of each reaction the uptake of hydrogen was a linear function of time, and the ratios of the initial reaction rates are shown in Table 1. It is apparent that increasing substitution in the alkoxy group reduces the rate of reaction.

Ethoxytrimethylsilane, isopropoxytrimethylsilane and tert-butoxytrimethylsilane were also reacted under the same conditions. After a small initial uptake of hydrogen no further diminution of volume occurred but examination of the solution

TABLE 1

RELATIVE INITIAL HYDROGENOLYSIS RATES

$Me_3SiOCPhMe_2$	Me_3SiOCH_2Ph	$Me_3SiOCHPh_2$	$Me_3SiOCHPhCH_3$
0.14	1.00	0.29	0.18

by GLC showed that reaction had in fact taken place and hexamethyldisiloxane was produced in each case. The constancy in volume of the gas phase was probably due to the fact that the hydrocarbon products were gaseous. Moreover it was found that once the initial diminution in volume had ceased, evacuation of the apparatus followed by the introduction of fresh hydrogen led to a further diminution in volume, which then died away in turn. This fact, and also the slow rates of reaction of these compounds, could be explained if the gaseous hydrocarbon products were only slowly released from the catalyst surface and were thus impeding the access of hydrogen to the reaction site.

The investigations were then extended to the hydrogenolysis of dialkoxysilanes. Diethoxydimethylsilane reacted extremely slowly and 20% of the starting material was still unreacted after 7 days. Approximately 30% of the dialkoxysilane had been converted to hexamethylcyclotrisiloxane, together with a small amount of octamethylcyclotetrasiloxane. Infrared spectroscopy of the non-volatile products showed the presence of hydroxyl groups, possibly associated with dimethylsiloxane diol or longer chain siloxane diols. Bis(benzyloxy)dimethylsilane reacted to yield cyclic trimer as the major product, a small amount of cyclic tetramer and a small amount of hydroxy compound. Bis(benzyloxy)diphenylsilane reacted to give diphenylsilanediol in approximately 50% yield and hexaphenylcyclotrisiloxane in approximately 40% yield. Both these products were isolated and fully characterised. No cleavage of 1-naphthylphenylmethylmethoxysilane was observed over a period of seven days. IR and NMR spectroscopic analysis of the products indicated that the naphthyl group had been partly hydrogenated.

EXPERIMENTAL

Chromatography and spectroscopy were carried out as described previously[6].

Preparations

The compounds were all prepared by dropwise addition of a solution of a chlorosilane in ether to a solution of an alcohol and pyridine in ether with stirring. The reaction mixture was worked up in the usual manner. The products had the following characteristics.

tert-Butoxytrimethylsilane: b.p. 100.5–102°; NMR (τ): 9.91, 8.72. The product was set aside for eleven months in a stoppered flask and the IR spectrum then showed a new broad band at 3100–3550 cm^{-1}.

(α,α-Dimethylbenzyloxy)trimethylsilane: b.p. 58°/2 mmHg: NMR(τ): 2.7–2.9, 8.62, 9.93.

(Benzyloxy)trimethylsilane: b.p. 52°/2 mmHg; NMR (τ): 2.65, 5.38, 9.91. After 13 months in a stoppered flask the product had separated into two liquid layers and a solid. These were separated and characterised by IR spectroscopy.

Isopropoxytrimethylsilane, fractionally distilled through a vigreux column, b.p. 77°. The IR spectrum was unchanged after four months in a stoppered flask.

(Diphenylmethoxy)trimethylsilane: b.p. 96°/0.3 mmHg; NMR (τ): 2.55–2.95, 4.20, 9.92. After ten months in a stoppered flask the IR spectrum showed new bands at 3100–3500 (broad) and 1710 cm^{-1}.

(α-Methylbenzyloxy)trimethylsilane: b.p. 45°/1 mmHg. After eight months in a stoppered flask the IR spectrum indicated extensive decomposition with a new broad band at 3100–3600 cm^{-1}.

Ethoxytrimethylsilane: b.p. 72°.

Diethoxydimethylsilane: b.p. 46.5°/74 mmHg.

Bis(benzyloxy)dimethylsilane: b.p. 123°/6 mmHg. After one month in a stoppered flask the IR spectrum showed a new band at 1705 cm^{-1}.

Bis(benzyloxy)diphenylsilane: b.p. 208°/0.25 mmHg.

Methanolysis reactions

A measured quantity (between 1 and 2 g) of alkoxysilane was dissolved in 25 ml dry methanol and stirred continuously at room temperature. Samples were removed at intervals and examined by GLC. The proportion of starting material remaining was determined from peak areas.

Hydrogenolysis reactions

The hydrogenations were carried out in a glass hydrogenation apparatus at room temperature and atmospheric pressure by stirring a solution of 0.01 mol alkoxysilane in 20 ml cyclohexane with 1 g of a 10% palladium on charcoal catalyst. In most cases the reaction could readily be followed by measuring the decrease in volume of the hydrogen. The reaction mixture was examined for volatile products by GLC against standard reference solutions. Solid products were isolated by removal of the solvent, followed by crystallisation, and characterised by IR spectroscopy.

ACKNOWLEDGEMENT

The authors thank Dow Corning (Barry) for the gift of chemicals.

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