REACTION OF p-(TRIMETHYLSILYL)BENZALDEHYDE WITH ORGANOMAGNESIUM COMPOUNDS

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We here report the continuation of our investigation of the properties of p-(trimethylsilyl)benzaldehyde and its derivatives. We have previously studied addition and condensation reactions of p-(trimethylsilyl)benzaldehyde with various organic substances [1, 2]. We have now examined the reaction of p-(trimethylsilyl)benzaldehyde with organomagnesium compounds. As a result we obtained silicon-containing aromatic secondary alcohols.

The preparation and properties of silicon-containing aromatic alcohols have formed the subject of a number of papers. Thus, Grütner and Cauer [3] synthesized secondary alcohols via p-(triethylsilyl)phenylmagnesium bromide and various aldehydes. New silicon-containing aromatic secondary alcohols were later synthesized by an analogous method by Winslow [4] and by Campagna and Post [5]. There is a reference to the possibility of preparing secondary alcohols of this class in a tetrahydrofuran medium via p-(trimethylsilyl)phenylmagnesium chloride [6]. α-Methyl-p-(trialkylsiloxy)benzyl alcohols have been prepared by organomagnesium synthesis by Golodnikov [7-9]. Another method for the preparation of silicon-containing aromatic secondary alcohols is the reduction of the corresponding ketones [6].

Alcohols of general formula

$$R_2Si(CH_2)_nCH(OH)CH_3,$$

in which $R = CH_3, C_2H_5, R' = H, CH_3; n = 0-2$, were prepared by Petrov, Chernyshev, and Tolstikova [10] by the reaction of the corresponding trialkylsilyl phenylmagnesium bromides with acetaldehyde and with acetone. However, the yields of the alcohols with $n = 1$ and $2$ were very small, and they, therefore, proposed to synthesize tertiary alcohols as follows [11]:

$$R_2Si(CH_2)_nCH_2COCl \xrightarrow{AlCl_3} R_2Si(CH_2)_nCOCH_3 \xrightarrow{CH_3MgBr} R_2Si(CH_2)_nCOH \rightarrow CH_3$$

Miller [12] prepared a tertiary alcohol containing two silicon atoms by the use of organolithium synthesis. Organosilicon alcohols derived from 1,4-dihydronaphthalene have been prepared by an analogous method [13]. Dihydric organosilicon aromatic alcohols have been prepared by Fleming [14] via organolithium compounds. Silicon-containing primary aromatic alcohols have been prepared by the reaction of [(triethylsilyl)phenyl]magnesium bromide with ethylene and propylene oxides [5].

Brannen [15, 16] proposed a new method for the introduction of functional groups into tetraarylsilanes with the aid of N-bromosuccinimide. He obtained p-(triphenylsilyl)benzyl alcohol as follows:

$$p \cdot (C_6H_5)_3SiC_6H_4CH_3 \xrightarrow{NBS, CCl_4} p \cdot (C_6H_5)_3SiC_6H_4CH_3Br \xrightarrow{AgNO_3, H_2O} p \cdot (C_6H_5)_3SiC_6H_4CH_3OH$$
Severson [17] brominated trimethyltolylsilanes with N-bromosuccinimide, converted the bromo compounds obtained into acetic esters, and hydrolyzed the latter to give o-, m-, and p-(trimethylsilyl)benzyl alcohols. We have reported [2] that p-(trimethylsilyl)benzyl alcohol is obtained by the condensation of p-(trimethylsilyl)benzaldehyde with formaldehyde in presence of alkalies and also by the Cannizaro reaction:

$$\text{2p-(CH}_3\text{)}_3 \text{SiCH}_3\text{CHO} \rightarrow \text{p-(CH}_3\text{)}_3 \text{SiC}_6\text{H}_4\text{CHO} + \text{p-(CH}_3\text{)}_3 \text{SiC}_6\text{H}_4\text{COOH}$$

We have now found that p-(trimethylsilyl)benzaldehyde reacts vigorously with organomagnesium compounds by Equation (1):

$$\text{p-(CH}_3\text{)}_3 \text{SiC}_6\text{H}_4\text{CHO} + \text{RMgX} \rightarrow \text{p-(CH}_3\text{)}_3 \text{SiC}_6\text{H}_4\text{CH}_2\text{OH} \quad \text{(1)}$$

in which R = CH₃, C₂H₅, C₆H₅, C₆H₅Si(CH₃)₃.

The same α-alkyl-p-(trimethylsilyl)benzyl alcohols were prepared also from p-(trimethylsilyl)phenylmagnesium bromide by Equation (2):

$$\text{p-(CH}_3\text{)}_3 \text{SiC}_6\text{H}_4\text{MgBr} + \text{RCHO} \rightarrow \text{p-(CH}_3\text{)}_3 \text{SiC}_6\text{H}_4\text{CHR} \quad \text{(2)}$$

in which R = CH₃, C₂H₅, C₆H₅.

It was found that in both cases [Equations (1) and (2)] the α-ethylbenzyl alcohol was obtained in the highest yield, and the α-methylbenzyl alcohol in the lowest yield. In all cases reaction in accordance with Equation (1) gave a yield of the alcohol that was higher by 10-20%. Prolonged heating of the reaction mixture and the introduction of a large excess of aldehyde in syntheses in accordance with (1) and (2) did not lead to an increase in the yield of silicon-containing alcohols.

On the basis of data in the literature, Shostakovskii and others [18] concluded that in the physicochemical properties of silicon-containing alcohols, the same relationships hold as in the case of their organic analogs. The chemical properties of these compounds are determined by the presence and position of the hydroxy group and the structures of the silicon-attached organic groups. Silicon-containing aromatic alcohols react with sodium with liberation of hydrogen [7, 8]. Tertiary alcohols of this class are readily reduced by lithium aluminum hydride to the corresponding silanes [12]; primary alcohols are oxidized to acids by treatment with potassium permanganate [16]. On reaction with acetone in presence of aluminum alkoxides, secondary alcohols are converted into ketones [19].

Most attention has been devoted to the dehydration of silicon-containing aromatic alcohols with the object of obtaining the corresponding styrenes. Thus, secondary alcohols are dehydrated into styrenes over activated alumina at temperatures of above 300° under reduced pressure [4, 10] and also on being boiled with potassium hydrogen sulfate [6]. Chernyshev, Petrov, and others [11] have shown that the tertiary alcohols

$$\text{R}_3\text{Si} \left(\text{CH}_3\right)_n \overset{\text{CH}}{\overset{\text{COHCH}_3}{\text{CH}_3}}$$

(n = 0, 1, 2) are dehydrated quantitatively when boiled with RSO₃ in the case of R = CH₃, but are more readily dehydrated over alumina at 340° in the case of R = C₂H₅. The styrenes obtained can polymerize with formation of high-melting polymers [20, 21].

The alcohols that we obtained — α-methyl-p-(trimethylsilyl)benzyl alcohol, α-ethyl-p-(trimethylsilyl)benzyl alcohol, and 4-(trimethylsilyl)benzhydrol — were viscous congealing liquids; 4,4'-bistrimethylsilylbenzhydrol was a crystalline substance, m.p. 104-105.5°. These alcohols are stable to the action of 20-50% acids. When α-methyl-p-(trimethylsilyl)benzyl alcohol and the original (p-bromophenyl)trimethylsilane are treated with concentrated sulfuric acid the Si-Cₘ bond is broken. Among the products of the breakdown of the former we found benzene, hexamethyldisiloxane, and a very small amount of benzaldehyde, and the products of the breakdown of the latter were hexamethyldisiloxane and bromobenzene. All the alcohols react quantitatively with methylmagnesium iodide. Active-hydrogen determinations and analyses on the alcohols gave results in good accord with the theoretical values. We carried out