FREE-RADICAL ADDITION REACTIONS WITH 1-, 2-, AND 3-ALKENYLSILANES

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Over several years Petrov and co-workers have synthesized various organosilicon compounds containing a double bond in the α, β, γ, and other positions with respect to silicon [1-11]. Qualitative and quantitative differences were noted in the reactivities of these alkenylsilanes in ionic addition reactions. In all cases organosilicon compounds in which the double bond was in the β position were exceptionally active in these reactions. The intensities of the characteristic double bond frequencies of alkenylsilanes in the Raman spectra were found to be least for an α double bond, greatest for a β double bond, and intermediate in value for a γ double bond. Comparison of the calculated and found molecular refractions for the compounds $R_3Si(CH_2)_nCH=CH_2$ showed that there was exaltation for allylsilanes, but none for compounds in which n = 0, 2, 3, 4 [11]. Such physical peculiaritiesof allylsilanes as enhanced intensity of the double bond lines in the Raman and infrared spectra, exaltation of molecular refraction, and higher reactivity in the above-mentioned reactions are probably to be explained by the presence of conjugation between the double bond and the Si—C bond in these compounds[11].

We undertook the present investigation of free-radical addition reactions with 1-, 2-, and 3-alkenylsilanes under comparable conditions to determine the possibilities of this reaction in synthesis and to confirm the occurrence of conjugation of the double bond of allylsilanes with the Si—C bond. Some scattered data exist in the literature on free-radical addition reactions with vinyl- and allyl-silanes. Burkard and Krieble [12] reported the addition of $HSiCl_3$ to trichlorovinylsilane in presence of a peroxide. There were later reports of the addition of trichlorosilane and of dichloromethylsilane to various trialkylvinyl- and dialkyldivinyl-silanes [13, 14]. The additions of halogenated methanes, ethanes, and propanes to vinylsilanes in presence of peroxides have also been carried out [15, 16]. In all these cases the yields of adducts were high, attaining 80%. There is also a reference by Sommer [17] to the addition of butyraldehyde to trimethylvinylsilane in presence of acetyl peroxide, though no information is given about the yield and constants of the adduct. In 1947 Burkhard and Krieble [12] reported the addition of $HSiCl_3$ to allyltrichlorosilane,in presence of acetyl peroxide,in 33% yield. There have been no reports about the free-radical addition reactions of 3-butenylsilanes.

We synthesized triethylvinylsilane, allyltriethylsilane, and 3-butenyldiethylmethylsilane by known methods. The reactions were carried out by heating the mixture in presence of benzoyl peroxide. For the addition we used butyraldehyde, benzaldehyde, carbon tetrachloride, and chloroform. The addition ofbutyraldehyde to triethylvinylsilane went in 60% yield. The reaction went satisfactorily also with benzaldehyde. In this case the yield of adduct was 23%. Good yields were obtained also in the addition of $HCCl_3$ and CCl_4 to triethylvinylsilane in presence of benzoyl peroxide (48% and 43.5%, respectively). The formation of the monomeric product was here accompanied by telomerization products, and a considerable amount of high-boiling substances containg Si and C was obtained.

A series of reactions with carbon tetrachloride, chloroform, butyraldehyde, and methyl formate were carried out with allyltriethylsilane. The reactions were carried out both at atmospheric pressure at 70-100° and under pressure in an autoclave at 150°. In all cases no positive result was obtained; the reactants were generally recovered unchanged. The benzoyl peroxide was converted into benzoic acid. The free-radical reactions with 3-butenyldiethylmethylsilane were carried out under the same conditions as those with triethylvinylsilane, i.e., with heating (80-170°) in presence of benzoyl peroxide at atmospheric pressure.

With benzaldehyde and butyraldehyde we obtained the corresponding ketones in 17 and 27% yield, i.e., in lower yield than in the case of triethylvinylsilane. With carbon tetrachloride and chloroform the corresponding adducts were formed in 78% and 72% yield. A certain amount of high-boiling substances (telomers) was also obtained. The higher yields of the CCl_4 and $CHCl_3$ adducts for 3-butenyldiethylmethylsilane than for triethylvinylsilane is to be explained by the fact that in the latter case a considerable amount of telomers was obtained, whereas in the former mainly monomer was obtained.

In 1956 Topchiev and co-workers [18] reported addition reactions of $HSiCl_3$ and of triphenylsilane with various allylsilanes in presence of benzoyl peroxide. It was found that almost no reaction occurs between $HSiCl_3$ and allyltrimethyl- and allyltriethyl-silanes in presence of benzoyl peroxide at 50°; reaction occurs only under severe conditions under pressure at 120°, but in this case the yield of adducts is only 2.5-10%. When the alkyl groups of trialkylallylsilanes are replaced by substituents of electronegative character (phenyl or chlorine), the yields of reaction products rise to 20-60%.

In the free-radical polymerization of 1-, 2-, and 3-alkenylsilanes it was shown also that 2-alkenylsilanes polymerize less readily than 1- and 3-alkenylsilanes [19]. Our results and data in the literature confirm, in our opinion, that a double bond in the β position to silicon is conjugated with the Si−C bond. Allylsilanes have a low tendency to participate in free-radical addition reactions, evidently because the unpaired electron of the free radical formed in the reaction($\mathrm{R + C{=}C{-}C{-}Si}\!< \rightarrow \mathrm{R{-}C{-}C{-}C{-}Si}\!\leqslant$) is conjugated with the Si−C bond. Such free radicals (those in which the unpaired electron is conjugated) have a high stabilization energy and hence show a reduced tendency to enter into chain propagation [20-22].

The greater success in carrying out the reaction with allyltrichlorosilane leads us to the view that a determining effect on the possibility of the conjugation of the Si−C bond with bonds in the β position is exerted by the character of the other groups or atoms attached to the silicon atom, which determine the electronic structure of the Si−C bond. It may be considered that, if silicon is attached to three chlorine atoms, the Si−C is much less capable of conjugation than if the silicon is attached to three methyl or ethyl groups.

EXPERIMENTAL

Triethylvinylsilane, allyltriethylsilane, and (3-butenyl)-diethylsilane were synthesized by known methods. The carrying out of free-radical addition reactions with triethylvinylsilane is described in [23].

Reaction of Aldehydes with (3-Butenyl)-diethylmethylsilane

A. Butyraldehyde. A mixture of 30 g (0.19 mole) of 3-butenyl-diethylmethylsilane and 49 g (1.18 moles) of butyraldehyde was prepared in a round-bottomed flask fitted with reflux condenser, thermometer, and dropping funnel. The mixture was heated to the boil, and in the course of two hours a solution of 1.5 g of benzoyl peroxide in 49 g (1.18 moles) of butyraldehyde was added dropwise. The mixture was heated at the boil for 50 hours, in the course of which 4.5 g of benzoyl peroxide was added in 0.5-g portions at regular intervals. The boiling point of the mixture rose from 80° to 92°. To remove benzoic acid formed in the reaction, the mixture was washed with sodium carbonate solution and with water. The mixture was dried and fractionated. Fractionation gave 12.2 g of 8-(diethylmethylsilyl)-4-octanone; b.p. 127-128° (3.5 mm); n_D^{20} 1.4470; d^{20} 0.8605; found MR 70.79; calculated MR 71.21. The melting point of the 2,4-dinitrophenylhydrazone was 134°. Yield 42% on the 3-butenyldiethylmethylsilane that reacted and 27% on the amount taken. Found: C 68.28; 68.23; H 12.06; 12.20; Si 12.44; 12.26%. $C_{13}H_{28}SiO$. Calculated: C 68.46; H 12.28; Si 12.28%.

B. Benzaldehyde. The reaction was carried out under the same conditions. The amounts taken were 30 g (0.19 mole) of 3-butenyldiethylmethylsilane and 102 g (0.95 mole) of benzaldehyde. The boiling point of the mixture kept in the range 170-180°. Fractionation gave 9.7 g of 5-(diethylmethylsilyl)-valerophenone; b.p. 163-164° (3.5 mm); n_D^{20} 1.5168; d_4^{20} 0.9726; found MR 81.47; calculated MR 82.06. Yield 32% on the 3-butenyldiethylmethylsilane that reacted and 18% on the amount taken. Found: C 73.13; 73.20; H 9.90; 9.86; Si 10.82; 10.94%. $C_{16}H_{26}SiO$. Calculated: C 73.32; H 9.92; Si 10.68%.

Reaction of CCl_4 and of $CHCl_3$ with (3-Butenyl)-diethylmethylsilane

A. Chloroform. The reaction was carried out under the same conditions. The amounts taken were 30 g (0.19 mole) of 3-butenyldiethylmethylsilane and 136 g (1.14 moles) of chloroform. In the course of 50 hours 5.5 g of benzoyl peroxide was added. The boiling point of the mixture rose from 80° to 95°. Fractionation gave 37.8 g (72%) of diethylmethyl-(5,5,5-trichloropentyl)-silane; b.p. 127-129° (3 mm); n_D^{20} 1.4647; d_4^{20} 1.0578; found MR 71.86; calculated MR 72.34%; Found: C 43.25; 43.38; H 7.62; 7.42; Si 10.33; 10.14; Cl 37.78; 37.95%. $C_{10}H_{21}SiCl_3$. Calculated: C 43.68; H 7.63; Si 10.15; Cl 38.54%. The yield was 72%.

B. Carbon Tetrachloride. The reaction was carried out under the same conditions. The amounts taken were 30 g (0.19 mole) of 3-butenyldiethylmethylsilane and 176 g (1.14 moles) of carbon tetrachloride. In the course of 50 hours 5.5 g of benzoyl peroxide was added. The boiling point of the mixture rose from 80° to 95°. Fractionation gave 46.3 g (78%) of diethylmethyl-(3,5,5,5-tetrachloropentyl) silane; b.p. 128-130° (3.5 mm); n_D^{20} 1.4860; d_4^{20} 1.1684; found MR 76.17; calculated MR 76.68; Found: C 38.46; 38.54; H 6.38; 6.33; Si 9.18; 9.23; Cl 45.20; 45.03%. $C_{10}H_{20}SiCl_4$. Calculated: C 38.70; H 6.46; Si 9.03; Cl 45.81%. The yield was 78%.

SUMMARY

1. Free-radical addition reactions proceed readily with vinyl- and 3-butenyl-silanes, but with difficulty with allylsilanes, which confirms the presence of conjugation between the Si–C bond and a double bond in the β position with respect to silicon.

2. A determining effect on the possibility of conjugation of the Si–C bond is exerted by the character of the other groups or atoms attached to silicon which determine the electron structure of the Si–C bond.

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