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Reaction of Hydrosylanes with Methacrylamide and Nitroalkenes

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Abstract—In the reaction of hydrochlorosilanes with methacrylamide along with addition polymerization was observed. Under the influence of hydrochlorosilanes, conjugated nitroolefines were reduced to form respective nitroso derivatives which could not be isolated due to the instability of the reaction mixtures.

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The addition of hydrosilanes to unsaturated compounds is widely used for the synthesis of silicon compounds in the preparative synthesis and in the industry. In this study we explored a possibility of addition of hydrosilanes to methacrylamide and nitroolefins.

In the reaction of methyldichlorosilane with methacrylamide in the presence of tetramethylethylendiamine and copper(I) chloride a formation was observed of a solid amorphous dark-yellow material. In its IR spectrum strong bands were revealed at 2400–2600 cm^{-1}, corresponding to the $C–N^+$ bonds, no bands at 930 cm^{-1} ($=CH_2$) and 2170 cm^{-1} (Si–H), weak bands at 1010 cm^{-1} (Si–OC), of the carbonyl group (1650 cm^{-1}), and of the double bond (1600 cm^{-1}). In the infrared spectrum of the methacrylamide there are bands at 930 cm^{-1} ($=CH_2$), 2800–3000 cm^{-1} (NH), a strong band at 1650 cm^{-1} (CO), and a band at 1600 cm^{-1} (C=C conjugated). Based on the IR spectrum and elemental analysis, to the obtained substance the formula may be ascribed:

$$[SiMeClCH_2CMe]_n[CH_2CM_3{-}C{=}O]_m,$$
$$\quad\quad|\quad\quad\quad\quad\quad\quad|$$
$$\quad C(O)N^+H_3Cl\quad\quad\quad NH_2$$

$$n{:}m = 1{:}1.$$

Trichlorosilane reacts similarly. Reactions with trichlorosilane and methyldichlorosilane proceed also without a catalyst, but the process of hydrosilylation proceeds to a lesser extent, the ratio *n:m* is 1:3 for a substance obtained in the reaction with trichlorosilane and 1:4 with methyldichlorosilane. Addition of 0.1% of hydroquinone has no effect on the process. With dimethylchlorosilane, methacrylamide does not react even in the presence of a catalyst, while CuCl is reduced to metallic copper.

It is presumable that the addition is possible with other types of conjugated olefins. However, at the reaction of 1-nitroprop-1-ene and 1-nitropent-1-ene with trichlorosilane in the absence of a catalyst at 50°C the evolution of hydrogen chloride occurred (1–1.5 mol per 1 mol of olefin), and the reaction mixture got green. After evacuation of volatile products and hydrogen chloride in a vacuum the residue represented a substance close by analysis to the adduct without hydrogen chloride, with methyldichlorosilane the data of analysis corresponded to a mixture of adduct and the adduct without hydrogen chloride. At the attempted distillation of the reaction mixture vigorous decomposition occurred. At keeping the reaction mixture over dry ice during a night occurred polymerization into a brittle resin insoluble in alcohol and toluene.

In the presence of the Speier's catalyst similar transformations were observed. With 2-nitrobut-2-ene, the trichlorosilane reacted similarly, but the coloration of the mixture after the synthesis remained turquoise. We presume that a reduction of the nitro group occurs with trichlorosilane to form a nitroso group followed by evolution of hydrogen chloride.

$$CH_3CH{=}CHNO_2 + HSiCl_3$$
$$\rightarrow CH_3CH{=}CHNO + HOSiCl_3.$$

The nitroso compound formed possess a hydrogen atom at the carbon α-atom and is rearranged into oxime [1], which can react with chlorosilane liberating hydrogen chloride, and this explains the large amount

of HCl, as well as the low content of chlorine and high content of silicon in the formed substance.

$$CH_3CH{=}CHNO \rightarrow CH_3CH{=}C{=}NOH$$

$$\xrightarrow{\geq SiCl} CH_3CH{=}C{=}NOSi{\leq} + HCl.$$

In the case of 2-nitrobut-2-ene the nitroso derivative has no hydrogen in the α-position and consequently cannot rearrange into oxime, therefore the reaction mixture to the end of the synthesis retains the turquoise color. It should be noted that hydrochlorosilane can be added to unconjugated nitroalkenes [2].

EXPERIMENTAL

Reaction of trichlorosilane with methacrylamide. Into a flask with a reflux condenser, thermometer, and dropping funnel was placed 0.2 mol of methacrylamide, 30 ml of anhydrous toluene, and through dropping funnel 0.3 mol of trichlorosilane was added. The mixture was heated to 65°C, a rapid boiling begun and good external cooling was needed to prevent ejection through condenser. Then the mixture was refluxed for 9 h. The final temperature was 80°C. After cooling, the liquid was decanted and 19.6 g (44.5%) of solid resin was obtained. After drying under vacuum 12.9 g of a substance was obtained not melting up to 250°C, insoluble in conventional organic solvents. Found, %: C 40.61, H 6.8, Cl 22.52, Si 5.92. $C_{16}H_{29}Cl_3N_4O_4Si$. Calculated, %: C 40.38, H 6.1, Cl 22.45, Si 5.89.

Reaction of methyldichlorosilane with methacrylamide. The synthesis was carried out similarly to the previous experiment, with the same amounts of reagents, but instead of trichlorosilane was used methyldichlorosilane. The mixture was at reflux for 13 h, the temperature slowly rose to 95°C. After cooling, the liquid was decanted. 19.4 g (48.5%) of solid resin was formed. After drying a solid substance of light yellow color formed, not melting up to 250°C, insoluble in conventional organic solvents. Found, %: C 46.96, H 7.61, Cl 16.15, Si 6.06. $C_{21}H_{39}Cl_2N_5O_5Si$. Calculated, %: C 46.67, H 7.22, Cl 13.14, Si 5.18.

Reaction of trichlorosilane with methacrylamide in the presence of a catalyst. To a flask was placed 2 g of copper(I) chloride, 4.8 ml of tetramethylethylendiamine, 0.2 mol of methacrylamide, and 30 ml of toluene. Gradually 0.3 mol of trichlorosilane was added. Self-heating to 60°C occurred. When the boiling finished, the mixture was cooled, the liquid was decanted, and 31.3 g (70.9%) of the resin was isolated. After drying, a solid was formed, not melting up to 250°C, insoluble in conventional organic solvents. Found, %: C 32.06, H 5.50, Cl 32.8, Si 10.48. $C_8H_{15}Cl_3N_2O_2Si$. Calculated, %: C 31.42, H 4.91, Cl 34.86, Si 9.16.

Reaction of methyldichlorosilane with methacrylamide in the presence of a catalyst. Similarly to the previous run, but instead of trichlorosilane methyldichlorosilane was used. At the addition a weak self-heating occurred, but after 10-min boiling begun a violent reaction with the formation of the resin. The boiling of the mixture was continued for another 2 h, the temperature increased from 80 to 110°C. 41.2 g (95.5%) of yellow solid was isolated. After drying the substance was not melting to 250°C and was not soluble in conventional solvents. Found, %: C 38.22, H 6.50, Cl 20.88, Si 10.70. $C_9H_{18}Cl_2N_2O_2Si$. Calculated, %: C 37.89, H 6.32, Cl 24.95, Si 9.82.

Reaction of trichlorosilane with 1-nitropent-1-ene. To 0.2 mol of 1-nitropent-1-ene was added 0.3 mol of trichlorosilane at room temperature. The temperature rose to 50°C, the mixture got green, then turned to brown, hydrogen chloride evolved even when cooling to 26°C. In total 0.35 mol of HCl evolved. 46.5 g (87.65%) of a mixture containing 42.3% of Cl formed.

Reaction of trichlorosilane with 1-nitropent-1-ene in the presence of a catalyst. To 0.1 mol of 1-nitropent-1-ene and 0.05 ml of Speier catalyst at 60°C was added 0.15 mol of trichlorosilane. Green color appeared, the temperature rose to 120°C; 23.7 g (94.8%) of a substance was obtained. Found, %: Cl 47.55, Si 12.7. After removing volatile component in a vacuum of 10 mm Hg (temperature in the mixture 70°C) 21 g (98.1%) of a substance was obtained. Found, %: Cl 42.56, Si 10.72. $C_5H_9Cl_2NO_2Si$. Calculated, %: Cl 42.51, Si 11.18. At an attempt to distillation, the substance decomposed vigorously; when it was stored overnight over dry ice it polymerized into glassy mass, insoluble in alcohol and toluene, soluble in concentrated alkali.

Reaction of methyldichlorosilane with 1-nitroprop-1-ene. To 0.2 mol of 1-nitroprop-1-ene with 0.05 ml of Speier catalyst was added 0.3 mol of methyldichlorosilane, the mixture was refluxed for 8 h, then volatile components were removed in a vacuum. 21.2 g (64.6%) of a substance was isolated. Found, %:

C 31.27, H 4.04, Cl 20.05, N 8.81, Si 18.57. $C_4H_8ClNO_2Si$. Calculated, %: C 29.00, H 4.83, Cl 21.45, N 8.45, Si 16.92.

Reaction of trichlorosilane with 2-nitrobut-2-ene. To 0.1 mol of 2-nitrobut-2-ene at 80°C was added trichlorosilane, the temperature rose to 142°C, the mixture got green. The mixture was cooled in a water bath and the rest of trichlorosilane was added at 60–70°C. 12.9 g (60.28%) of a substance was obtained. Found, %: C 25.27, H 4.04, Cl 32.73, N 6.54, Si 14.83. $C_4H_7Cl_2NO_2Si$. Calculated, %: C 24.00, H 3.50, Cl 35.50, N 7.00, Si 14.00

Reaction of trichlorosilane with 2-nitrobut-2-ene in the presence of a catalyst. Similarly to the previous run, to 0.1 mol of 2-nitrobut-2-ene in the presence of the Speier catalyst was added 0.05 ml of trichlorosilane at 30°C, the temperature rose to 50°C. After cooling, volatile components were removed in a vacuum; 17.8 g (88.7%) of turquoise substance with the Cl content of 32.78% was isolated.

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