REACTION OF CARBOXYLIC ACID FLUORIDES AND PERFLUOROPROPYLENE OXIDE WITH (ACYLOXYMETHYL)DIMETHYLETHOXYSILANES

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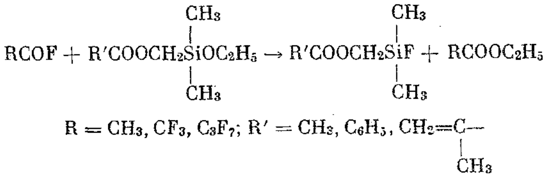
Previously [1, 2] it was shown that when carboxylic acid chlorides or bromides are reacted with organosilicon compounds that contain acetoxymethyl and ethoxy groupings on the silicon atom the alkyl–oxygen bond of the acetate group is cleaved and either chloro- or bromomethylsilanes are formed. In the present paper we studied the reaction of the acid fluorides of the acetic, trifluoroacetic, and perfluorobutyric acids with the (acetoxymethyl)-, (benzoyloxymethyl)-, and (methacryloyloxymethyl)dimethyl-ethoxysilanes.

In contrast to the acid chlorides and bromides, replacement of the alkoxy group by fluorine, which is usual [3, 4] for alkoxysilanes, was observed for the acid fluorides, which probably can be explained by the greater tendency to form the Si–F bond

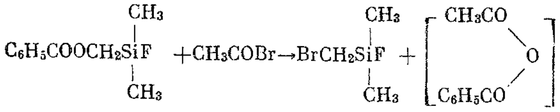


$$\mathrm{RCOF} + \mathrm{R'COOCH_2\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}OC_2H_5} \rightarrow \mathrm{R'COOCH_2\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}F} + \mathrm{RCOOC_2H_5}$$

$$\mathrm{R = CH_3, CF_3, C_3F_7;\ R' = CH_3, C_6H_5, CH_2{=}\underset{\displaystyle CH_3}{C}{-}}$$

This reaction makes it possible to obtain organosilicon compounds that simultaneously contain an ester grouping in the hydrocarbon radical and a fluorine atom attached directly to silicon, which represent interest for the modification of polymeric materials. The structure of the obtained compounds was confirmed by the IR and ^{19}F NMR spectra, by titration of the hydrolyzable fluorine, and by elemental analysis. The structure of the radical of the ester group has no effect on the value of the chemical shifts in the ^{19}F NMR spectrum, and their values are close to those for the fluorosilanes [4].

In contrast to the unfluorinated acid fluorides, the perfluorocarboxylic acid fluorides react with the evolution of heat, i.e., they are much more reactive due to their greater electrophilicity. The obtained (acyloxymethyl)dimethylfluorosilanes react with acid chlorides and bromides in the same manner as the (acyloxymethyl)dimethylethoxysilanes [1], i.e., the acyloxy group is replaced by halogen. Thus, the reaction of acetyl bromide with (benzoyloxymethyl)dimethylfluorosilane gave bromomethyldimethylfluorosilane in good yield



$$\mathrm{C_6H_5COOCH_2\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}F} + \mathrm{CH_3COBr} \rightarrow \mathrm{BrCH_2\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}F} + \left[\begin{array}{c}\mathrm{CH_3CO}\\ \qquad\diagdown\\ \qquad\quad \mathrm{O}\\ \qquad\diagup\\ \mathrm{C_6H_5CO}\end{array}\right]$$

The acid fluorides do not enter into similar reactions even when heated up to 150°C. Fluoromethyldimethylfluorosilane could be obtained only by heating (160°) (benzoyloxymethyl)dimethylfluorosilane with perfluoropropylene. The mechanism of this replacement is probably analogous to that proposed earlier [5] for the reactions of perfluoropropylene oxide with electrophilic reagents

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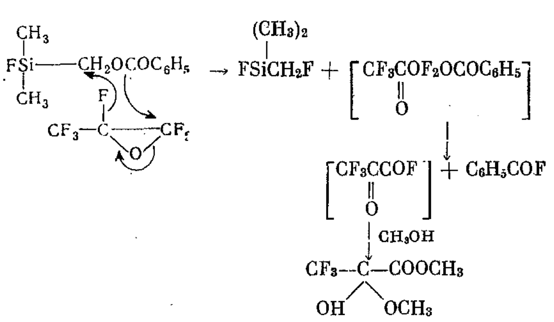

EXPERIMENTAL METHOD

The ^{19}F NMR spectra were taken on a Hitachi R-20 spectrometer (56.46 MHz). The chemical shifts are given in ppm from CF_3COOH. The IR spectra were taken on a UR-20 spectrophotometer.

(Acetoxymethyl)dimethylfluorosilane. 1. A mixture of 7.0 g (0.04 mole) of (acetoxymethyl)dimethylethoxysilane and 2.5 g (0.04 mole) of CH_3COF was heated in a sealed glass ampule on the water bath for 10 h. Distillation gave 3 g (52%) of (acetoxymethyl)dimethylfluorosilane, bp 130°; 79-80° (120 mm); n_D^{20} 1.3840; d_{20}^{20} 1.060. Found: C 39.16; H 7.19; Si 18.24; F 12.42 (hydrolyzable)%; MR 33.50. $C_{15}H_{11}FO_2Si$. Calculated: C 40.01; H 7.33; Si 18.66; F 12.65%; MR 35.39. ^{19}F NMR spectrum: 79.4 m (SiF). Infrared spectrum: 1730 (C=O), 850 cm^{-1} (SiF).

2. In a flask, equipped with a reflux condenser, cooled with solid CO_2, and a gas-inlet tube, was placed 4.4 g (0.025 mole) of (acetoxymethyl)dimethylethoxysilane, and 3.5 g (0.03 mole) of CF_3COF was passed in slowly; here the temperature of the mass rose to 40°. Vacuum-distillation at first, followed by distillation at atmospheric pressure, gave 2.7 g (76.5%) of $CF_3CO_2C_2H_5$, bp 60-63° [5], and 3 g (80%) of (acetoxymethyl)dimethylfluorosilane, bp 130°; n_D^{20} 1.3840.

3. In a flask was placed 9.7 g (0.055 mole) of (acetoxymethyl)dimethylethoxysilane, and 12 g (0.055 mole) of perfluorobutyryl fluoride was passed in slowly; here the temperature rose to 60°. Distillation gave 13 g (98%) of ethyl perfluorobutyrate, bp 96°; n_D^{20} 1.307; d_{20}^{20} 1.38 [6], which was identified chromatographically by comparison with an authentic specimen, and 5.5 g (67%) of (acetoxymethyl)dimethylfluorosilane, bp 130°; n_D^{20} 1.3840.

(Benzoyloxymethyl)dimethylfluorosilane. In the same manner as the preceding, from (benzoyloxymethyl)dimethylethoxysilane and perfluorobutyryl fluoride we obtained (benzoyloxymethyl)dimethylfluorosilane in 81% yield, bp 100° (10 mm); n_D^{20} 1.4870; d_{20}^{20} 1.090. Found: C 56.56; H 6.19; Si 12.81; F 8.77 (hydrolyzable)%; MR 56.01. $C_{10}H_{13}FO_2Si$. Calculated: C 56.60; H 6.14; Si 13.19; F 8.97%; MR 55.12. ^{19}F NMR spectrum: 78.2 (SiF). Infrared spectrum: 1720 (C=O), 850 cm^{-1} (SiF).

(Methacryloyloxymethyl)dimethylfluorosilane. In a similar manner, from (methacryloyloxymethyl)-dimethylethoxysilane and perfluorobutyryl fluoride we obtained (methacryloyloxymethyl)dimethylfluorosilane in 85% yield, bp 70-73° (23 mm); n_D^{20} 1.4155; d_{20}^{20} 1.021. Found: C 46.84; H 7.33; F 11.20; Si 14.519%. MR 43.3. $C_7H_{13}FO_2Si$. Calculated: C 47.70; H 7.39; F 10.79; Si 15.90%; MR 44.2. ^{19}F NMR spectrum: 80.86 (SiF). Infrared spectrum: 1640 (C=C), 850 cm^{-1} (SiF).

(Bromomethyl)dimethylfluorosilane. With stirring, to 10.6 g (0.05 mole) of (benzoyloxymethyl)dimethylfluorosilane was added 7 g (0.056 mole) of CH_3COBr; here the temperature of the mass rose to 35°, and heating was continued on the water bath for 2 h. Distillation gave 7.1 g (83%) of (bromomethyl)dimethylfluorosilane, bp 97-99°; n_D^{20} 1.4172; d_{20}^{20} 1.372. Found: C 21.03; H 4.88; F 9.89; Br 45.09; Si 14.74%; MR 31.40. C_3H_8BrFSi. Calculated: C 21.05; H 4.67; F 11.11; Br 46.78; Si 16.37%; MR 32.04. ^{19}F NMR spectrum: 82.6 (SiF). Infrared spectrum: 565 and 640 (CBr), 880 cm^{-1} (SiF).

(Fluoromethyl)dimethylfluorosilane. In a 50 ml steel ampule, cooled with solid CO_2, were placed 14 g (0.066 mole) of (benzoyloxymethyl)dimethylfluorosilane and 11 g (0.07 mole) of perfluoropropylene oxide. The ampule was heated at 160° for 12 h, after which it was cooled and connected to a trap, cooled to −50°. Passage of the fraction from the trap (2 mm) through absolute methanol gave 1.2 g of methyl α-hydroxy-α-methoxyperfluoropropionate, which was identified by comparison with an authentic specimen [7] employing GLC and the ^{19}F NMR spectrum.

Distillation of the product from the ampule gave 5 g (66%) of (fluoromethyl)dimethylfluorosilane, bp 53°; n_D^{20} 1.3130. Found: C 32.62; H 7.22; F 33.76; Si 23.61%. $C_3H_8F_2Si$. Calculated: C 32.70; H 7.27;

F 34.48; Si 25.46%. ^{19}F NMR spectrum: 89.8 m (SiF), 200 t (CH_2F), J_{FCH_2} = 48.5 Hz). In addition, 3 g of C_6H_5COF with bp 150° was isolated.

CONCLUSIONS

1. In contrast to the acid chlorides and bromides, when carboxylic and perfluorocarboxylic acid fluorides are reacted with (acyloxymethyl)dimethylethoxysilanes only the ethoxy group on the silicon atom is replaced by fluorine.

2. The formed (acyloxymethyl)dimethylfluorosilanes when reacted with acetyl bromide replace the acyloxy group by the bromine atom to give bromomethyldimethylfluorosilane.

3. (Fluoromethyl)dimethylfluorosilane was obtained by heating an (acyloxymethyl)dimethylfluorosilane with perfluoropropylene oxide.

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