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Abstract

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ORGANOSILICON COMPOUNDS OF THE FURAN SERIES

ORGANOSILICON DERIVATIVES OF FURYLCARBINOLS

AND 5-SUBSTITUTED FURFURYL ALCOHOLS

In the preceding communication (^{1}) it was shown that furfuryloxysilanes can be synthesized by the reaction of furfuryl alcohol with alkylchlorosilanes in the presence of pyridine. In the present work the reaction of trialkylchlorosilanes with furylalkyl- and furylarylcarbinols was investigated:

$$\text{furyl-}CH(OH)R + R_3'SiCl \xrightarrow{C_5H_5N} \text{furyl-}CH(OSiR_3')R + C_5H_5N \cdot HCl \quad (1)$$

\end{equation}

where $R = CH_3;\ C_2H_5;\ C_3H_7;\ C_6H_5, \quad R' = CH_3;\ C_2H_5$.

In the reaction of 5-nitrofurfuryl alcohol with trimethylchlorosilane in the presence of pyridine, the first representative of organosilicon nitrofurans, 5-nitrofurfuryloxytrimethylsilane, was synthesized.

$$5\text{-}O_2N\text{-furyl-}CH_2OH + (CH_3)_3SiCl \xrightarrow{C_5H_5N} 5\text{-}O_2N\text{-furyl-}CH_2OSi(CH_3)_3 + C_5H_5N \cdot HCl \quad (1a)$$

\end{equation}

Earlier (^{1}) we carried out the dehydrocondensation of hydrosilanes with furfuryl alcohol in the presence of catalytic amounts of sodium. In the present work, in the reaction of hydrosilanes with furfuryl alcohol, 5-methylfurfuryl alcohol, and furylalkylcarbinols, a decimolar solution of chloroplatinic acid in absolute isopropyl alcohol was successfully used as the catalyst*:

$$\text{furyl-}C(H)(OH)(R')R + HSiR''R_2''' \longrightarrow \text{furyl-}CH(OSiR''R_2''')(R')R + H_2 \quad (2)$$

where $R = CH_3;\ H, \quad R' = CH_3;\ C_2H_5;\ C_3H_7;\ H,$

$$R'' = CH_3;\ C_2H_5;\ C_2H_5O;\ (C_2H_5)_2SiOH, \qquad R''' = C_2H_5;\ C_3H_7;\ C_2H_5O.$$

The catalyst is added in a minute amount: 10^{-5} mole per 1 mole of alcohol. By this route, furfuryloxysilanes are obtained in purer form and in higher yield than by the methods we developed earlier (^{1}). The reaction can be carried out at room temperature. This makes it possible to avoid the transesterification of triethoxysilane by furfuryl alcohol and thereby to obtain triethoxyfurfuryloxysilane:

$$\text{furyl-}CH_2OH + HSi(OC_2H_5)_3 \longrightarrow \text{furyl-}CH_2OSi(OC_2H_5)_3 + H_2 \qquad (2a)$$

Since at room temperature hydrosilanes do not dissolve in furfuryl alcohol, and their interaction in the heterogeneous phase proceeds slowly, the reaction was usually carried out at 80–100°. The constants of the obtained–

* The reaction of alcohols with compounds containing the $Si—H$ bond, in addition to H_2PtCl_6 (^{2,3}) and alcoholates ($^{4—12}$), is also catalyzed by organic bases (^{13,14}), metallic copper ($^{11,15—18}$), and metal chlorides ($^{19—24}$).

furfuryloxysilanes; their yields and analytical data are given in Table 1.

Alcohols introduced into the reaction with hydrosilanes must be thoroughly dehydrated, since, in the presence of water, chloroplatinic acid causes the conversion of hydrosilanes into silanols (26).

Experimental Part

The reaction of furylcarbinols with chlorosilanes in the presence of pyridine was carried out by the method described (1). 5-Nitrofurfuryloxysilane was synthesized by a somewhat different procedure.

Synthesis of 5-nitrofurfuryloxytrimethylsilane. Into a four-necked flask equipped with a mechanical stirrer, two dropping funnels, and a reflux condenser protected by a calcium chloride tube, a solution of 20.03 g (0.14 mole) of 5-nitrofurfuryl alcohol in 100 ml of dry ether is placed. The flask is cooled with ice water and, with stirring, from the two dropping funnels there are simultaneously added a solution of 11 g (0.14 mole) of pyridine in 23 ml of ether and a solution of 15.2 g (0.14 mole) of trimethylchlorosilane in 25 ml of ether, at such a rate that during the addition of the reagents there is a slight excess of trimethylchlorosilane in the reaction mixture. Thereafter the reaction mixture is stirred for 2 hours at room temperature. The precipitate of pyridine hydrochloride is filtered off and washed with ether. The ether, unreacted trimethylchlorosilane, and pyridine are distilled off at

Table 1

Furfuryloxysilanes

R	R	Obtained according to scheme	B.p., °C	Pressure, mm Hg	n_D^{20}	d_4^{20}	MR_D, calculated	MR_D, found	Si, %, calculated	Si, %, found	Yield, %
H	CH OSiCH (C H)	2	77–79	9	1.4533	0.9369	57.28	57.24	14.15	14.34; 14.23	87
H	CH OSi(C H)	2	95–96	7	1.4600	0.9423	61.79	61.71	13.21	13.43; 13.31	90
H	CH OSi(OC H) *	2	115–116	10	1.4300	1.0405	64.43	64.63	10.77	10.75; 10.73	31
H	CH OSi(C H) OSi(C H) OC H	2	177–180	3	1.4690	1.0424	102.92	102.20	14.67	14.94; 15.08	41
CH	CH OSiCH (C H)	2	100–102	12	1.4579	0.9354	61.94	61.93	13.22	13.01; 13.15	75
CH	CH OSiCH (C H)	2	104–106	6	1.4570	0.9086	71.41	70.77	11.56	11.34; 11.51	70
CH	CH OSi(C H)	2	107–108	5	1.4540	0.9488	66.42	66.32	12.40	12.12; 12.21	89
CH	CH OSi(C H)	2	109–110	15	1.4570	0.9336	66.42	66.03	12.40	12.28; 12.18	70.5
H	CH(CH)OSi(C H)	1	85–87	25	1.4428	0.9267	57.52	56.75	14.13	13.00; 13.71	68
H	CH(C H)OSi(C H)	1,2	113–115	10	1.4564	0.9262	71.05	70.60	11.67	11.73; 11.69	40(1), 51(2)
H	CH(C H)OSi(C H)	1	75–76	10	1.4481	0.9233	62.15	61.62	13.20	13.09; 13.04	25
H	CH(C H)OSi(C H)	2	105–107	4	1.4582	0.9204	75.65	75.38	10.98	10.69; 10.52	38
H	CH(C H)OSi(C H)	1	117–119	5	1.5200	1.0253	72.65	73.01	11.35	10.82; 10.98	31.8
H	CH(C H)OSi(CH)	1	100	2	1.4998	1.1218	56.11	56.53	13.04	13.08; 12.96	70
O N	CH OSi(CH)										

* Literature data (25): according to scheme 1, b.p. 85.5–86.5° (3).

under reduced pressure. From the residue, 26.8 g (70%) of 5-nitrofurfuryloxytrimethylsilane with b.p. 100° (2 mm) is obtained.

Reaction of alcohols with hydrosilanes in the presence of H_2PtCl_6.

The syntheses of furfuryloxysilanes were carried out by the following procedure. To 3 ml of hydrosilane, one drop (0.014 ml) of a 0.1 M solution of $H_2PtCl_6 \cdot 6H_2O$ in absolute isopropyl alcohol is added, the mixture is heated to boiling, and the remaining amount of hydrosilane (0.1 mole in all) and 0.1 mole of the corresponding alcohol are added. The mixture is heated at 80–100° (depending on the temperature of the hydrosilane) until the evolution of hydrogen ceases. The furfuryloxysilane formed is isolated and purified by vacuum distillation.

Hydrolysis of triethylsilane. To 5.8 g (0.05 mole) of triethylsilane, one drop of a 0.1 M solution of $H_2PtCl_6 \cdot 6H_2O$ in absolute iso-C_3H_7OH is added, the mixture is heated to boiling, and 20 ml of dioxane containing 0.9 g (0.05 mole) of water is added. After the evolution of hydrogen ceases, the dioxane is distilled off. From the residue, 6.0 g (90%) of triethylsilanol is obtained, with b.p. 153–155°; n_D^{20} 1.4330; d_4^{20} 0.8650, which agrees with literature data ([27]).

When the experiment was carried out under analogous conditions, but with a molar ratio $(C_2H_5)_3SiH : H_2O$ not of 1 : 1 but of 2 : 1, the yield of triethylsilanol (from 5.8 g of triethylsilane) was 5.1 g, or 77%.

Reaction of triethylsilane with triethylsilanol. To 3.3 g (0.028 mole) of triethylsilane, a drop of catalyst and 3.7 g (0.028 mole) of triethylsilanol are added. Even on heating to boiling for 12 h, no hydrogen was evolved. Distillation gave 3 g (90.9%) of triethylsilane, 1.9 g of triethylsilanol, and 1.3 g of hexaethyldisiloxane, which is the product of anhydrocondensation of triethylsilanol under the influence of H_2PtCl_6.

Thus, 5-nitrofurfuryloxytrimethylsilane—the first representative of silicon-containing nitrofurans—has been synthesized. The reaction of furfuryl alcohol, 5-methylfurfuryl alcohol, and furylalkylcarbinols with hydrosilanes in the presence of catalytic amounts of H_2PtCl_6 has been studied. By this route, a series of new furfuryloxysilanes has been synthesized. It has been shown that triethylsilane reacts with water in dioxane medium in the presence of H_2PtCl_6 to form triethylsilanol.

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REFERENCES CITED

[1] E. Lukevits, Yu. Romadan, S. Geller, *Izv. AN LatvSSR*, No. 7, 59 (1961). [2] Engl. pat. 842672 (1960); *Chem. Abstr.*, **55**, 1066 (1961). [3] G. H. Barnes, G. W. Scheitzer, Pat. USA, 2967171 (1961). R. N. Meals, *J. Am. Chem. Soc.*, **68**, 1880 (1946). W. H. Nebergall, *J. Am. Chem. Soc.*, **72**, 4702 (1950). H. Kautsky, E. Daubach, *Zs. Naturforsch.*, **56**, 443 (1950). A. F. Reitly, H. W. Post, *J. Org. Chem.*, **16**, 383 (1951). S. Nitzsche, *Angew. Chem.*, **83**, 490 (1951). J. S. Peake, W. H. Nebergall, Y. T. Chen, *J. Am. Chem. Soc.*, **74**,

1526 (1952). [1] N. S. Nametkin, A. V. Topchiev, L. S. Povarov, *DAN*, **99**, 403 (1954). [11] B. N. Dolgov, N. P. Kharitonov, M. G. Voronkov, *ZhOKh*, **24**, 1178 (1954). [12] B. N. Dolgov, N. P. Kharitonov, T. V. Tsukshverdt, *ZhOKh*, **28**, 2714 (1958). [13] Engl. pat. 707564 (1954); *RZhKhim.*, 2295 (1956). [1] H. Gilman, G. E. Dunn et al., *J. Am. Chem. Soc.*, **77**, 1287 (1955). [1] W. S. Miller, J. S. Peake, W. H. Nebergall, *J. Am. Chem. Soc.*, **79**, 5604 (1957). [1] B. Sternbach, A. G. MacDiarmid, *J. Am. Chem. Soc.*, **81**, 5109 (1959). [1] B. Sternbach, A. G. MacDiarmid, *J. Am. Chem. Soc.*, **83**, 3384 (1961). [1] B. O. Reikhsfeld, V. A. Prokhorova, *ZhOKh*, **31**, 2613 (1961). [1] S. Nitzsche, E. Pirson, FRG patent 900497 (1953), *RZhKhim.*, 30370 (1955). [2] R. Decker, H. Holz, Fr. pat. 1040941 (1953), *RZhKhim.*, 38492 (1955). [21] Engl. pat., 707587 (1954), *RZhKhim.*, 2295 (1956). [22] M. G. Voronkov, V. N. Zgonnik, *ZhOKh*, **27**, 1479 (1957). [23] B. N. Dolgov, Yu. I. Khudobin, N. P. Kharitonov, *Izv. AN SSSR, OKhN*, 1958, 113. [2] B. N. Dolgov, N. P. Kharitonov et al., *ZhOKh*, **28**, 2710 (1958). [2] D. F. Peppard, W. G. Brown, W. C. Johnson, *J. Am. Chem. Soc.*, **68**, 70 (1946). [2] E. Ya. Lukevits, M. G. Voronkov, *Izv. AN LatvSSR, Ser. Khim.*, 2, 127 (1961). [2] Ya. I. Ryskin, M. G. Voronkov, *ZhFKh*, **30**, 2245 (1956), **24**, 3816 (1959).

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