REACTION OF TRIALKYLSILANES WITH PENTAFLUOROPHENOL

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Trialkylsilanes in the presence of an I_2–Al mixture, Lewis acids, and certain metals, enter into the dehydrocondensation reaction with mono- and polyhydric phenols by the scheme:

$$nR_3SiH + (HO)_nC_6H_{6-n} \rightarrow (R_3SiO)_nC_6H_{6-n} + nH_2$$

where n = 1-3 [1-5]. The reaction of trialkylsilanes with pentafluorophenol was studied in the present paper (Tables 1 and 2).

The trialkylsilanes do not react with pentafluorophenol, either in the absence of a catalyst or in the presence of C_6F_5ONa, anhydrous $SnCl_2$ or $ZnCl_2$ (see Table 1). Increasing the reaction temperature up to 146°C also does not lead to the desired result. In the presence of an I_2–Al mixture the reaction proceeds with the quantitative evolution of H_2, but the yield of $R_3SiOC_6F_5$ does not exceed 50%. Of the investigated catalysts the best proved to be colloidal Ni, which was obtained by the reduction of anhydrous $NiCl_2$ with the appropriate trialkylsilane [3-7]. In the presence of this catalyst the trialkylsilanes react with pentafluorophenol without the formation of side products, in which connection the yields of the trialkyl(pentafluorophenoxy)silanes are 96-99% (see Table 2). We synthesized 13 trialkyl(pentafluorophenoxy)silanes. Compounds of the indicated type were previously unknown. The trialkyl(pentafluorophenoxy)silanes are colorless liquids with a peculiar odor. Their boiling points and refractive indices are lower, while the density is higher than for the corresponding trialkylphenoxysilanes.

EXPERIMENTAL METHOD

The trialkylsilanes were obtained by the reaction of the apropriate alkylmagnesium halides and hydrochlorosilanes in ether. Their properties are described in [1, 4, 6-8]. The physical constants and analysis

TABLE 1. Reaction of Trialkylsilanes with Pentafluorophenol*

R_3SiH	Catalyst	Amount of catalyst, mole (atom) %	Reaction temperature, °C	Reaction time, h	Yield, %	
					H_2	$R_3SiOC_6F_5$
$(C_2H_5)_3SiH$	—	—	109—110	24	0	0
$(C_2H_5)_3SiH$	C_6F_5ONa	5	109—110	24	0	0
$(C_2H_5)_3SiH$	$SnCl_2$	6,4	109—128	48	0	0
$(C_2H_5)_3SiH$	$Al + I_2$	6,4	108—196	0,5	100	49,3
$(C_2H_5)_3SiH$	Ni	2	110—218	1	100	98,8
$(n\text{-}C_3H_7)_3SiH$	C_6F_5ONa	5	146—148	24	0	0
$(n\text{-}C_3H_7)_3SiH$	$SnCl_2$	6,4	146—148	24	0	0
$(n\text{-}C_3H_7)_3SiH$	$ZnCl_2$	6,4	146—148	24	0	0
$(n\text{-}C_3H_7)_3SiH$	Ni	2	146—235	1,25	100	97,6

*In all of the experiments the mole ratio was $R_2SiH:HOC_6F_5$ = 1:1.

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TABLE 2. Properties of Trialkyl(pentafluorophenoxy)silanes $R_3SiOC_6F_5$

R_3Si	Yield, %	Bp, °C (p, mm of Hg)	d_4^{20}	n_D^{20}	Found			Empirical formula	Calculated		
					MR	mol. wt.	Si, %		*MR*	mol. wt.	Si, %
$(C_2H_5)_3Si$	98,8	218—219(765)	1,1984	1,4365	65,16	298,1	9,42	$C_{12}H_{15}F_5O_1Si_1$	63,26	298,34	9,41
$n\text{-}C_4H_9(CH_3)_2Si$	97,8	217,5—218(767)	1,1299	1,4278	67,91	297,7	9,37	$C_{12}H_{15}F_5O_1Si_1$	63,26	298,34	9,41
$(n\text{-}C_3H_7)_3Si$	97,6	99—100(3)	1,1398	1,4423	79,06	342,4	8,27	$C_{15}H_{21}F_5O_1Si_1$	77,20	340,42	8,25
$CH_3(n\text{-}C_4H_9)_2Si$	98,2	104,5(3)	1,1141	1,4390	80,38	340,3	8,20	$C_{15}H_{21}F_5O_1Si_1$	77,20	340,42	8,25
$n\text{-}C_7H_{15}(CH_3)_2Si$	98,4	107,5(2,5)	1,1116	1,4361	80,11	341,4	8,26	$C_{15}H_{21}F_5O_1Si_1$	77,20	340,42	8,25
$(n\text{-}C_4H_9)_3Si$	97,5	124,5(2,5)	1,0874	1,4460	93,81	380,7	7,33	$C_{18}H_{27}F_5O_1Si_1$	91,14	382,50	7,34
$C_2H_5(n\text{-}C_5H_{11})_2Si$	96,9	130(3)	1,0907	1,4463	93,58	381,2	7,31	$C_{18}H_{27}F_5O_1Si_1$	91,14	382,50	7,34
$n\text{-}C_{10}H_{21}(CH_3)_2Si$	98,7	125,5(2,8)	1,0885	1,4415	92,89	383,1	7,30	$C_{18}H_{27}F_5O_1Si_1$	91,14	382,50	7,34
$(n\text{-}C_5H_{11})_3Si$	97,4	151(3)	1,0612	1,4488	107,27	423,8	6,62	$C_{21}H_{33}F_5O_1Si_1$	105,09	424,58	6,62
$(n\text{-}C_6H_{13})_3Si$	98,6	174(2,5)	1,0455	1,4514	120,29	465,7	6,03	$C_{24}H_{39}F_5O_1Si_1$	119,03	466,66	6,02
$(n\text{-}C_7H_{15})_3Si$	98,2	197(3)	1,0223	1,4534	134,64	507,9	5,65	$C_{27}H_{45}F_5O_1Si_1$	132,98	508,75	5,62
$(n\text{-}C_8H_{17})_3Si$	97,9	217,5(2,5)	1,0073	1,4557	148,55	552,3	5,11	$C_{30}H_{51}F_5O_1Si_1$	146,94	550,83	5,10
$(n\text{-}C_9H_{19})_3Si$	98,5	249(2,5)	0,9917	1,4572	162,92	593,7	4,76	$C_{33}H_{57}F_5O_1Si_1$	160,86	592,91	4,74

TABLE 3. Properties of Alkyldimethylsilanes $R(CH_3)_2SiH$

R	Bp, °C (p, mm of Hg)	d_4^{20}	n_D^{20}	Found			Empirical formula	Calculated, %			Yield, %
				MR	mol. wt.	Si, %		MR	mol. wt.	Si, %	
n-C_6H_{13}	99,5—100 (762)	0,7179	1,4028	39,51	115,5	24,20	$C_8H_{20}Si$	39,76	116,28	24,76	68
n-C_7H_{15}	172—173 (768)	0,7492	1,4218	53,70	157,9	17,71	$C_9H_{22}Si$	53,70	158,36	17,74	73
n-$C_{10}H_{21}$	74 (2,5)	0,7705	1,4337	67,70	200,3	14,07	$C_{12}H_{28}Si$	67,65	200,44	14,01	77

data for the previously unknown alkyldimethylsilanes are given in Table 3. The pentafluorophenol was purified by fractional distillation and had bp 143° (751 mm). We describe one the syntheses as an example.

Triethyl(pentafluorophenoxy)silane. A mixture of 5.8 g (0.05 mole) of triethylsilane, 9.2 g (0.05 mole) of pentafluorophenol, and 0.06 g of colloidal Ni, obtained by the reduction of 0.13 g of anhydrous $NiCl_2$ with triethylsilane, was heated until the H_2 evolution ceased (30 min). Here the temperature of the reaction mixture rose from 110 to 218° and 1.24 liters (100%) of H_2 was evolved. Distillation of the reaction mixture gave 14.7 g (98.8%) of triethyl(pentafluorophenoxy)silane with bp 217-220° (765 mm). After redistillation it had the constants indicated in Table 2.

CONCLUSIONS

A study was made of the catalytic reaction of trialkylsilanes with pentafluorophenol, which leads to the formation of the previously unknown trialkyl(pentafluorophenoxy)silanes in up to 99% yield. Colloidal Ni proved to be the best catalyst for this reaction.

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