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Abstract

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SYNTHESIS AND PROPERTIES OF MONO-, DI-, AND TRI-*p*-TOLYLALKYLSILANES

In recent years a large number of works have been published describing methods for obtaining and the properties of silicon hydrocarbons of various structures. Derivatives of silicon hydrocarbons containing functional groups in the organic radical have, up to the present time, scarcely been studied; they may be of both theoretical and practical interest. It seemed of interest to us to obtain silicon hydrocarbons with *p*-tolyl radicals and to study the possibilities of synthesizing, on their basis, compounds with functional groups in the organic radical.

Silicon hydrocarbons with *p*-tolyl radicals have scarcely been investigated. The literature describes tetra-*p*-tolylsilane ((^{1,2})), tri-*p*-tolylsilane ((^3)), phenyl-*p*-tolylsilanes ((^{4,5})), and naphthyl-*p*-tolylsilanes ((^{6-8})). Of the alkyl-*p*-tolyl derivatives of silicon, only tri-*p*-tolylmethylsilane ((^3)), di-*p*-tolyldimethylsilane ((^9)), *p*-tolyltrimethylsilane ((^{10,11})), and *p*-tolyltriethylsilane ((^{12})) have been described.

In the present communication we describe mono-, di-, and tri-*p*-tolylalkyl derivatives of silicon, the properties of which are given in Tables 1 and 2.

p-Tolylchloro(ethoxy)silanes

p-Tolyltrichlorosilane and di-*p*-tolyldichlorosilane were obtained from silicon tetrachloride and *p*-tolylmagnesium bromide and, in their properties, correspond to the literature data ((^{13-15})).

p-Tolyltriethoxysilane (Table 1), di-*p*-tolyldiethoxysilane (Table 1), and tri-*p*-tolylethoxysilane (Table 2) were obtained from tetraethoxysilane and *p*-tolylmagnesium bromide.

p-Tolyldipropylethoxysilane was isolated from the reaction products in the synthesis of di-*p*-tolyldipropylsilane (see below and Table 1).

p-Tolyldiisobutylethoxysilane was obtained by the interaction of isobutyllithium with *p*-tolyltriethoxysilane. Into the reaction were taken 45 g (0.33 mole) of isobutyl bromide, 5.6 g (0.8 mole) of lithium, and 22 g (0.09 mole) of *p*-tolyltriethoxysilane. The reaction mixture was heated for 10 hr; 9.5 g (yield 38.8%) of *p*-tolyldiisobutylethoxysilane was obtained (Table 1).

Mono-, di-, and tri-*p*-tolylalkylsilanes

** *p*-Tolyltrimethylsilane.** To *p*-tolyllithium, prepared from 8.4 g of lithium and 94 g of *p*-bromotoluene, 54.5 g of trimethylchlorosilane was added. The mixture was heated for 8 hr. 58.2 g was obtained (yield 71%).

** *p*-Tolyltriethylsilane.** To ethyllithium, prepared from 3.2 g of lithium and 21.8 g of ethyl bromide, 12 g of *p*-tolyltriethoxysilane was added. The mixture was heated for 10 hr. 5.5 g was obtained (yield 56.6%).

** *p*-Tolyltripropylsilane.** To propyllithium, prepared from 6 g of lithium and 44.3 g of propyl bromide, 23 g of *p*-tolyltrichlorosilane was added. The mixture was heated for 10 hr. 10.8 g was obtained (yield 43.2%).

** *p*-Tolyltributylsilane.** To *p*-tolyllithium, prepared from 3.5 g of lithium and 34 g of *p*-bromotoluene, 38 g of tributylethoxysilane was added. The mixture was heated for 10 hr. 34 g was obtained (yield 73%).

Table 1

Compound formula	b.p., °C/mm Hg	d_4^{20}	n_D^{20}	MR_D, found	MR_D, calc.	Found, % C	Found, % H	Calculated, % C	Calculated, % H
$p\text{-}CH_3C_6H_4Si(CH_3)_3$	190–193/756	0.8651	1.4908	54.98	54.58	73.26 73.14	9.87 9.76	73.12	9.82
$p\text{-}CH_3C_6H_4Si(C_2H_5)_3$	92–93/3	0.8897	1.5025	68.53	68.47	75.70 75.61	10.73 10.75	75.65	10.74
$p\text{-}CH_3C_6H_4Si(C_3H_7)_3$	121–122/4	0.8764	1.4952	82.68	82.46	77.71 77.86	11.13 11.14	77.35	11.36
$p\text{-}CH_3C_6H_4Si(C_4H_9)_3$	154–156/5	0.8706	1.4922	96.77	96.25	78.29 78.44	12.15 12.31	78.60	11.80
$p\text{-}CH_3C_6H_4Si(i\text{-}C_5H_{11})_3$	148–150/2	0.8649	1.4862	110.35	110.14	79.59 79.62	12.09 12.20	79.45	12.11
$(p\text{-}CH_3C_6H_4)_2Si(CH_3)_2$	128–130/2	0.9700	1.5520	79.13	78.88	80.61 80.71	8.47 8.34	79.97	8.36
$(p\text{-}CH_3C_6H_4)_2Si(C_2H_5)_2$	145–147/3	0.9643	1.5520	88.95	88.22	80.52 80.57	9.08 9.14	80.55	9.01
$(p\text{-}CH_3C_6H_4)_2Si(C_3H_7)_2$	179–180/4	0.9382	1.5428	98.43	97.40	81.35 81.35	9.53 9.44	81.11	9.45
$(p\text{-}CH_3C_6H_4)_2Si(C_4H_9)_2$	194–195/5	0.9400	1.5375	107.52	106.66	81.53 81.43	9.91 9.74	81.45	9.94
$(p\text{-}CH_3C_6H_4)_2Si(i\text{-}C_4H_9)_2$	174–176/3	0.9485	1.5345	106.47	106.66	80.75 80.56	10.07 10.14	81.45	9.94
$(p\text{-}CH_3C_6H_4)_2Si(i\text{-}C_5H_{11})_2$	180–182/2	0.9304	1.5308	117.14	115.92	81.28 81.31	10.04 10.04	81.50	10.03
$p\text{-}CH_3C_6H_4Si(C_3H_7)_2(OC_2H_5)$	96–100/2	0.9139	1.4897	79.18	78.59	72.98 72.81	10.47 10.46	72.00	10.48

Compound formula	b.p., °C/mm Hg	d_4^{20}	n_D^{20}	MR_D, found	MR_D, calc.	Found, % C	Found, % H	Calculated, % C	Calculated, % H
$(p\text{-}CH_3C_6H_4)Si(i\text{-}C_4H_9)_2(OC_2H_5)$	137–138/8	0.9089	1.4892	88.45	87.75	73.31 73.39	10.86 10.85	73.32	10.86
$p\text{-}CH_3C_6H_4Si(OC_2H_5)_3$	115–117/7	0.9832	1.4664	71.71	70.75	61.79 61.87	7.73 8.84	61.49	8.70
$(p\text{-}CH_3C_6H_4)_2Si(OC_2H_5)_2$	150–152/4	1.0148	1.5262	90.90	89.66	72.29 72.22	8.20 8.04	72.01	8.06

Table 2

Compound formula	b.p., °C/mm Hg	m.p., °C	Found, % C	Found, % H	Calculated, % C	Calculated, % H
$(p\text{-}CH_3C_6H_4)_3Si\text{–}CH_3$	197–200/4	91.5–92.5	83.55 83.53	7.76 7.71	83.49	7.64
$(p\text{-}CH_3C_6H_4)_3Si\text{–}C_2H_5$	190–192/2	72	83.29 83.49	8.14 8.18	83.58	7.93
$(p\text{-}CH_3C_6H_4)_3Si\text{–}C_3H_7$	206–208/4	54.5–55	83.74 83.58	8.34 8.31	83.66	8.19
$(p\text{-}CH_3C_6H_4)_3Si\text{–}C_4H_9$	214–216/4	47.5–48	83.83 83.83	8.39 8.37	83.74	8.43
$(p\text{-}CH_3C_6H_4)_3Si\text{–}i\text{-}C_4H_9$	197–199/3	68–69	83.70 83.64	8.46 8.53	83.74	8.43
$(p\text{-}CH_3C_6H_4)_3Si\text{–}i\text{-}C_5H_{11}$	205–207/3	49–50	83.77 83.79	8.88 8.71	83.58	8.90
$(p\text{-}CH_3C_6H_4)_3Si\text{–}OC_2H_5$	194–195/3	50–50.5	79.52 79.77	7.61 7.52	79.68	7.56

***n*-Tolyltriisoamylsilane.** To isoamyllithium, prepared from 6.5 g of lithium and 53.8 g of isoamyl bromide (1-bromo-3-methylbutane), 17.7 g of *n*-tolyltrichlorosilane was added. The mixture was heated for 8 hr. Obtained: 10.7 g (yield 41%).

Di-*p*-tolyldimethylsilane. To *p*-tolyl lithium, prepared from 35.4 g of lithium and 425 g of *p*-bromotoluene, 129 g of dimethyldichlorosilane was added. The mixture was heated for 8 h. Yield: 160 g (67%).

Di-*p*-tolyldiethylsilane. To *p*-tolyl lithium, prepared from 13 g of lithium and 115 g of *p*-bromotoluene, 50 g of diethyldichlorosilane was added. The mixture was heated for 8 h. Yield: 67 g (78.6%).

Di-*p*-tolyldipropylsilane. To *p*-tolyl lithium, prepared from 7 g of lithium and 70 g of *p*-bromotoluene, 34 g of dipropyldiethoxysilane was added. The mixture was heated for 8 h. Yield: 16 g (32.7%).

During distillation of the reaction mixture, 9 g of *p*-tolyldipropylethoxysilane was also isolated (yield 21.7%).

Di-*p*-tolyldibutylsilane. To *p*-tolyl lithium, prepared from 10.5 g of lithium and 114 g of *p*-bromotoluene, 71.4 g of dibutyldibromosilane was added. The mixture was heated for 8 h. Yield: 52 g (71.2%).

Di-*p*-tolyldiisobutylsilane. To a mixture of *p*-tolylmagnesium bromide, prepared from 27 g of magnesium and 180 g of *p*-bromotoluene, and isobutylmagnesium bromide, prepared from 27 g of magnesium and 140 g of isobutyl bromide, 85 g of silicon tetrachloride was added. The mixture was heated for 10 h. Yield: 26 g (16%).

Di-*p*-tolyldiisoamylsilane. To isoamyl lithium, prepared from 4 g of lithium and 32.5 g of isoamyl bromide, 20 g of di-*p*-tolyldichlorosilane was added. The mixture was heated for 8 h. Yield: 9.5 g (38%).

Tri-*p*-tolylmethylsilane. To methylmagnesium iodide, prepared from 15 g of magnesium and 56 g of methyl iodide, 50 g of tri-*p*-tolylethoxysilane was added. After the ether had been distilled off, the reaction mixture was heated for 10 h at 100°. Yield: 18 g (39.5%).

Tri-*p*-tolylethylsilane. To *p*-tolyl lithium, prepared from 10 g of lithium and 102 g of *p*-bromotoluene, 32.8 g of ethyltrichlorosilane was added. The mixture was heated for 10 h. Yield: 35 g (53%).

Tri-*p*-tolylpropylsilane. To propyl lithium, prepared from 12 g of lithium and 90 g of propyl bromide, 70 g of tri-*p*-tolylethoxysilane was added. The mixture was heated for 10 h. Yield: 23 g (33.1%).

Tri-*p*-tolylbutylsilane. To butyl lithium, prepared from 4 g of lithium and 34 g of butyl bromide, 25 g of tri-*p*-tolylethoxysilane was added. The mixture was heated for 8 h. Yield: 13 g (50.4%).

Tri-*p*-tolylisobutylsilane. To *p*-tolyl lithium, prepared from 8.75 g of lithium and 85.5 g of *p*-bromotoluene, 33 g of isobutyltriethoxysilane was added. After the ether had been distilled off, the reaction mixture was heated for 10 h at 100°. Yield: 23 g (43%).

Tri-*p*-tolylisoamylsilane. To isoamyl lithium, prepared from 1 g of lithium and 6.5 g of isoamyl bromide, 15 g of tri-*p*-tolylethoxysilane was added. The mixture was heated for 8 h. Yield: 7 g (43.5%).

All tri-*p*-tolylalkylsilanes were recrystallized from ethyl alcohol.

Moscow Petroleum Institute
named after I. M. Gubkin

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