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Abstract

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SYNTHESIS OF CERTAIN ORGANOSILICON AND TITANIUM-ORGANOSILICON COMPOUNDS

In investigating the influence of triaryl-, trialkyl-, and mixed tri(alkylaryl)siloxy groups on the properties of titanium–organosilicon compounds, we were faced with the need to synthesize certain new titanium–organosilicon derivatives containing aromatic and aliphatic radicals at the silicon atom. Earlier, methods for the synthesis of tetrakis(trimethylsiloxy)titanium ([1,2]) and tetrakis(triphenylsiloxy)titanium ([3,4]) had been described in the literature. To obtain mixed tetrakis(tri(arylalkyl)siloxy)titaniums, we synthesized a series of organosilicon compounds that served as starting materials for the preparation of tetrakis(tri(alkylaryl)siloxy)titaniums. Phenyldimethylchlorosilane and methyldiphenylchlorosilane were obtained by the Grignard reaction. In order to obtain alkylarylsilanols, these compounds were converted into acetates and then hydrolyzed with ammonia solutions. The general reaction scheme for obtaining alkylarylsilanes may be represented by the following equations:

I. $C_6H_5MgBr + C_6H_5CH_3SiCl_2 \rightarrow (C_6H_5)_2CH_3SiCl + MgBrCl$;

II. $(C_6H_5)_2CH_3SiCl + CH_3COOK \rightarrow (C_6H_5)_2CH_3SiOCOCH_3 + KCl$;

III. $(C_6H_5)_2CH_3SiOCOCH_3 + NH_4OH \rightarrow CH_3(C_6H_5)_2SiOH + CH_3COONH_4$.

All compounds obtained according to this reaction scheme were isolated at each stage of the process, and their elemental composition and main constants were established. The properties of the synthesized substances are given in Table 1.

Table 1

Name of substance	Formula of substance	B.p., °C/mm Hg	n_D^{20}	d_4^{20}	MR, found	MR, calc.	Yield, %
Methyldiphenylchlorosilane	$CH_3(C_6H_5)_2SiCl$	153/10	1.5742	1.1277	68.4	69.06	54.4
Dimethylphenylchlorosilane	$(CH_3)_2C_6H_5SiCl$	100/33	1.5184	1.0646	48.8	49.93	63.3
Methyldiphenylacetoxysilane	$CH_3(C_6H_5)_2SiOCOCH_3$	135/2	1.5530	1.0756	75.95	75.91	51.2
Dimethylphenylacetoxysilane	$(CH_3)_2C_6H_5SiOCOCH_3$	95/7	1.5007	1.0065	55.79	55.78	59.1
Methyldiphenylsilanol	$CH_3(C_6H_5)_2SiOH$	134/2	1.5812	1.0829	65.80	66.42	67.8
Dimethylphenylsilanol	$(CH_3)_2C_6H_5SiOH$	195/7	1.5108	0.9848	46.11	46.10	65.1
Tetrakis-(methyldiphenylsiloxy)titanium	$[CH_3(C_6H_5)_2SiO]_4Ti$	378–380/1	1.5960	1.1248	273.4	274.8	35.8
Tetrakis-(dimethylphenylsiloxy)titanium	$[(CH_3)_2(C_6H_5)SiO]_4Ti$	275/7	1.5392	1.0533	193.97	193.476	51.9

The preparation of tetrakis-(tri(alkylaryl)siloxy)titanes was carried out by two methods. On treating diphenylmethylsilanol with titanium tetrachloride in the presence of ammonia,

$$4\,(C_6H_5)_2CH_3SiOH + TiCl_4 + 4\,NH_3 \rightarrow [(C_6H_5)_2CH_3SiO]_4Ti + 4\,NH_4Cl$$

tetrakis-(diphenylmethylsiloxy)titanium was obtained; it was a high-boiling liquid at room temperature.

Tetrakis-(dimethylphenylsiloxy)titanium was obtained by the reaction of sodium dimethylphenylsilanolate with titanium tetrachloride according to the scheme:

$$2\,(CH_3)_2C_6H_5SiOH + 2\,Na \rightarrow 2\,(CH_3)_2C_6H_5SiONa + H_2;$$

$$4\,(CH_3)_2C_6H_5SiONa + TiCl_4 \rightarrow [(CH_3)_2C_6H_5SiO]_4Ti + 4NaCl.$$

The properties of the synthesized compounds are given in Table 1.

Experimental Part

Dimethylphenylchlorosilane. A three-necked flask equipped with a stirrer, reflux condenser, and thermometer was charged with 12 g of magnesium and 200 ml of ethyl ether. From a dropping funnel, a solution of 87 g of bromobenzene in 50 ml of ethyl ether was introduced into the flask. The temperature was maintained at 34–38° until the magnesium had dissolved completely. The resulting Grignard reagent was added to a solution of 77 g of dimethyldichlorosilane in 70 ml of ethyl ether. The reaction proceeded at 38–44°. After decanting the reaction product from the precipitate, it was distilled. A fraction with b.p. 97–100°/33 mm was isolated in an amount of 63.68 g (yield 63.3% of theory).

Found, %: Cl 20.5

$C_8H_{11}SiCl$. Calculated, %: Cl 20.8.

Methyldiphenylchlorosilane. The synthesis of methyldiphenylchlorosilane was carried out analogously to the synthesis of dimethylphenylchlorosilane. From 157 g of bromobenzene, 24 g of magnesium, and 191 g of methylphenylchlorosilane, after vacuum distillation a fraction with b.p. 146–153°/10 mm was isolated; yield 125.15 g (54.4% of theory).

Literature data (5, 6): methyldiphenylchlorosilane, b.p. 180–195°/45 mm.

Found, %: Cl 15.9

$C_{13}H_{13}SiCl$. Calculated, %: Cl 15.3.

Methyldiphenylacetoxysilane. A three-necked flask was charged with 9.8 g of potassium acetate in 100 ml of dry toluene. From a dropping funnel, 23.25 g of methyldiphenylchlorosilane was added at a temperature of 18–28°. The mixture was then stirred and heated at 70–80° for 18–20 h. The KCl precipitate was filtered off, the solvent was distilled off, and the remaining liquid was distilled in vacuo at 132–135°/2 mm. Yield 12.95 g (51.2% of theory); n_D^{20} 1.5530; d_4^{20} 1.0756; found MR 75.95; calculated MR 75.91.

Found, %: C 70.32; H 6.84; Si 10.86

$C_{15}H_{16}O_2Si$. Calculated, %: C 70.31; H 6.25; Si 10.93.

Dimethylphenylacetoxysilane. It was obtained analogously from 63.68 g of dimethylphenylchlorosilane and 42 g of potassium acetate in 150 ml of dry toluene. Vacuum distillation gave 57.17 g of dimethylphenylacetoxysilane with b.p. 92–95°/7 mm. Yield 59% of theory; n_D^{20} 1.4907; d_4^{20} 1.0065; found MR 55.79; calculated MR 55.78.

Found, %: C 61.43; H 7.28; Si 14.08

$C_{10}H_{14}O_2Si$. Calculated, %: C 61.85; H 7.22; Si 14.40.

Methyldiphenylsilanol. Into a beaker equipped with a stirrer, thermometer, and dropping funnel were charged 100.5 ml of 15% NH_4OH (specific gravity 0.944) and 120 ml of ether. The mixture was cooled with ice to 0° and this temperature was maintained throughout the reaction. From the dropping funnel, with stirring, 96.6 g of methyldiphenylacetoxysilane in 100 ml of ether was added over 30–40 min. After completion of the addition of the acetate, stirring was continued for another 40–50 min, after which the layers were separated. The ether layer was washed twice with water (60 ml) and dried over ignited Na_2SO_4. After distilling off the ether, the residue was fractionated under vacuum. Fractionation gave a fraction with b.p. 130–134°/2 mm, yield 54.26 g (67.8% of theory); n_D^{20} 1.5812; d_4^{20} 1.0829; found MR 65.80; calculated MR 66.42.

Found, %:	C 72.98; H 6.84; Si 13.00
$C_{13}H_{14}OSi$. Calculated, %:	C 72.89; H 6.54; Si 13.07.

Dimethylphenylsilanol. It was obtained analogously by hydrolysis of 57 g of dimethylphenylacetoxysilane in 80 ml of 15% NH_4OH (specific gravity 0.944). Distillation gave a fraction with b.p. 192–197°/7 mm, yield 29.02 g (65.1% of theory); n_D^{20} 1.5108; d_4^{20} 0.9848; found MR 46.11; calculated MR 46.10.

Found, %:	C 63.17; H 8.09; Si 18.01
$C_8H_{13}OSi$. Calculated, %:	C 63.15; H 8.00; Si 18.42.

Sodium dimethylphenylsilanolate. Into a three-necked flask equipped with a stirrer, thermometer, and reflux condenser were charged 27 g of silanol in 30 ml of dry benzene. Metallic sodium, 4.05 g, was gradually added to the flask in pieces; the reaction proceeded with evolution of heat at 49–51°. After addition of one-third of the total amount of sodium, the temperature fell to 25°. The reaction mass was heated at 50° for 2 h. The remaining sodium, amounting to 2.4 g, was filtered off. The resulting solution of sodium silanolate was used directly for subsequent syntheses. The yield of silanolate was 44% of theory. The concentration of the solution was determined by titration of an aliquot with 0.1 N HCl.

Tetrakis-(methyldiphenylsiloxy)titanium. Into a three-necked flask with a stirrer, reflux condenser, and tube for introducing ammonia were charged 12.84 g of methyldiphenylsilanol in 180 ml of dry benzene. The mixture was cooled with ice to a temperature of 0–2°. With stirring and passage of NH_3, 2.85 g of $TiCl_4$ in 20 ml of dry benzene was added dropwise to the flask. The mixture at first became bright yellow; then, on further addition of $TiCl_4$, this color disappeared. After completion of the dropwise addition of $TiCl_4$, ammonia was passed for another 30 min, then the solution was heated for 3 h to remove excess ammonia. The precipitate was filtered off and the benzene distilled off. The residue—a viscous yellow liquid—was distilled under vacuum; a fraction with b.p.

370–374°/6 mm was collected, yield 4.05 g (35.8% of theory); n_D^{20} 1.5960; d_4^{20} 1.1248; found MR 273.4; calculated MR 274.8.

Found, %:	C 69.19; H 6.68; Si 12.51; Ti 5.33
$C_{52}H_{52}OSi_4Ti$. Calculated, %:	C 69.40; H 5.78; Si 12.43; Ti 5.33.

Tetrakis-(dimethylphenylsiloxy)titanium. Into a three-necked flask were charged 24 g of a 25% benzene solution of sodium dimethylphenylsilanolate. To this, 1.64 g of $TiCl_4$ in 10 ml of dry benzene was slowly added dropwise. The reaction proceeded with heating to 28–42°. The dropwise addition of $TiCl_4$ was continued until the medium was neutral. The massive NaCl precipitate was filtered off and the benzene was distilled from the filtrate.

On vacuum distillation of the remaining liquid, a fraction with b.p. 274–275°/7 mm was collected, yield 2.7 g (51.9% of theory); n_D^{20} 1.5392; d_4^{20} 1.0533; found MR 193.97; calculated MR 193.476.

$C_{32}H_{44}O_4Si_4Ti$.

Found, %: C 59.00; H 7.54; Si 16.81; Ti 6.71
Calculated, %: C 58.99; H 6.75; Si 17.18; Ti 7.36.

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Note: Figure translations are in progress. See original paper for figures.