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Abstract

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BROMO AND ACETOXY DERIVATIVES OF DIHYDRIDO-*p*-PHENYLENEDISILANES

In our work (1) we reported the synthesis of silicon hydrocarbons with a phenylene bridge, of the general formula

$$-\mathrm{Si}-(\mathrm{CH}_2)_n-\mathrm{Si}\left\langle\mathrm{C}_6\mathrm{H}_4\right\rangle\mathrm{Si}-(\mathrm{CH}_2)_n-\mathrm{Si}-\qquad(n=2\text{ and }3)$$

by the addition of dihydrido-*p*-phenylenedisilanes to vinyl- and allyltrialkylsilanes.

In the present work, in order to elucidate the reactivity of the Si—H bonds and to obtain *p*-phenylenedisilanes with other reactive groups, the bromination and acetylation reactions of dihydrido-*p*-phenylenedisilanes were studied.

The literature describes the replacement of hydrogen atoms in aromatic silicon hydrides by bromine through the direct action of bromine (2-7). At the same time, bromine, being one of the strong electrophilic reagents, cleaves the Si—C-phenyl bond on interaction with phenylsilanes (8-10). The degree of cleavage of Si—C-phenyl bonds in phenylsilanes under the action of bromine depends on the nature of the other radicals attached to silicon, as well as on the conditions under which the bromination reaction is carried out—the temperature of the reaction mixture, the catalyst used, the presence of a solvent, etc. (11, 12). Thus, bromine, on heating in the presence of FeBr_3 as a catalyst, readily cleaves 1,4-bis(triethylsilyl)benzene; the final products of this reaction are dibromobenzene and triethylbromosilane (10).

We carried out the replacement of hydrogen atoms by bromine in dihydrido-*p*-phenylenedisilanes by the action of bromine in carbon tetrachloride solution at a temperature of 0—(−3°):

$$\mathrm{H}-\mathrm{Si}\left\langle\mathrm{C}_6\mathrm{H}_4\right\rangle\mathrm{Si}-\mathrm{H}+\mathrm{Br}_2\rightarrow\mathrm{Br}-\mathrm{Si}\left\langle\mathrm{C}_6\mathrm{H}_4\right\rangle\mathrm{Si}-\mathrm{Br}$$

$$1)\ R=R'=\mathrm{C}_2\mathrm{H}_5;\quad 2)\ R=\mathrm{CH}_3,\ R'=\mathrm{C}_6\mathrm{H}_5;\quad 3)\ R=R'=\mathrm{C}_6\mathrm{H}_5.$$

Along with bromination of the dihydrido-*p*-phenylenedisilanes at both Si—H bonds, partial cleavage of the Si—C-phenyl bonds occurred. Some cleavage products were isolated—diethyldibromosilane (12.2%) in the case of bromination of 1,4-bis(diethylsilyl)benzene, and methylphenyldibromosilane (7.3%) in the case of 1,4-bis(methylphenylsilyl)benzene.

The yields of dibromo derivatives of dihydrido-*p*-phenylenedisilanes decrease as alkyl radicals in the latter are replaced by phenyl radicals (61.2; 52.0 and 31.5%, respectively), which is caused by cleavage by bromine not only of the grouping

$$-\mathrm{Si}\,\langle \mathrm{C_6H_4}\rangle\,\mathrm{Si}-$$

but also of the additionally introduced Si—C-phenyl bonds.

The starting 1,4-bis(diethyl)- and 1,4-bis(methylphenylsilyl)benzenes were synthesized by the organomagnesium method in ether medium from *p*-dibromobenzene (1). 1,4-Bis(diphenylsilyl)benzene was obtained in 52% yield according to the scheme:

$$\mathrm{Br}\,\langle \mathrm{C_6H_4}\rangle\,\mathrm{Br} + 2\mathrm{Mg} + 2(\mathrm{C_6H_5})_2\mathrm{SiHCl} \xrightarrow{\mathrm{THF}} \mathrm{H}(\mathrm{C_6H_5})_2\mathrm{Si}\,\langle \mathrm{C_6H_4}\rangle\,\mathrm{Si}(\mathrm{C_6H_5})_2\mathrm{H}.$$

Substitution of hydrogen atoms in silicon hydrides by the group —OOCR has been the subject of only a few works (13-16). In 1954, B. N. Dolgov, N. P. Kharitonov, and M. G. Voronkov (16) first used the reaction of catalytic interaction of trialkylsilanes with monocarboxylic acids for the preparative synthesis of acyloxysilanes. When a mixture of Al and I_2 was used as catalyst, high yields of acyloxysilanes (up to 87%) were obtained. The hydrogen atom bonded to silicon in trialkylsilanes is also readily replaced by an acyloxy group with the aid of mercury salts of organic acids:

$$\mathrm{R_3SiH} + \mathrm{Hg(OCOR')_2} \rightarrow \mathrm{R_3SiOCOR'} + \mathrm{Hg} + \mathrm{R'COOH}.$$

In order to obtain paraphenylene derivatives of silicon with acetoxy groups, we studied the reaction of dihydridoparaphenylenedisilanes with acetic anhydride in the presence of zinc chloride as catalyst:

$$\mathrm{H{-}Si(R)(R'){-}C_6H_4{-}Si(R)(R'){-}H} + (\mathrm{CH_3COO})_2\mathrm{O} \rightarrow \mathrm{CH_3CO{-}O{-}Si(R)(R'){-}C_6H_4{-}Si(R)(R'){-}O{-}COCH_3}$$

1) $R = R' = C_2H_5$; 2) $R = CH_3$; $R' = C_6H_5$

Substitution of hydrogen by the acetoxy group under the selected conditions proceeded at both Si—H bonds. The yields of 1,4-bis(diethyl)- and 1,4-bis(methylphenylacetoxysilyl)benzenes are 59.6 and 61.0%, respectively.

It was not possible to isolate the acetoxy derivatives from the reaction of dihydridoparaphenylenedisilanes with acetic acid in the presence of a mixture of Al and I_2, evidently because of quantitative cleavage of the Si—C-phenyl bond by iodine and aluminum iodide formed during the reaction.

Some physicochemical properties of bromo- and acetoxy derivatives of dihydridoparaphenylenedisilanes are presented in Table 1.

Dibromoparaphenylenedisilanes were subsequently used as starting products for the synthesis of

Table 1

Bromo- and acetoxy derivatives of dihydridoparaphenylenedisilanes

Compound	Boiling point, °C/mm Hg	Melting point, °C	d_4^{20}	n_D^{20}	MRD found	MRD calculated	Mol. wt. found	Mol. wt. calculated	C found, %	H found, %	Si found, %	Br found, %	C calculated, %	H calculated, %	Si calculated, %	Br calculated, %
$Br(C_2H_5)_2Si—C_6H_4—Si(C_2H_5)_2Br$	175–178/2		1.3221	1.5400	97.51	97.03	415	417	—	—	—	39.21	—	—	—	39.21
$Br(CH_3)(C_6H_5)Si—C_6H_4—Si(C_6H_5)(CH_3)Br$	248–250/3	61–62					480	486	—	—	—	33.20; 33.30	—	—	—	33.61
$Br(C_6H_5)_2Si—C_6H_4—Si(C_6H_5)_2Br$		197–198					571	578	60.23; 60.33	4.17; 3.83	9.29; 9.10	25.60; 25.50	60.0	4.00	9.34	26.60
$CH_3COO(C_2H_5)_2Si—C_6H_4—Si(C_2H_5)_2OOCCH_3$	174.5–175/3		1.0381	1.4903	103.45	102.35	366	368	58.94; 58.90	8.18; 8.18	15.26; 15.15	—	58.98	8.25	15.31	—
$CH_3COO(CH_3)(C_6H_5)Si—C_6H_4—Si(C_6H_5)(CH_3)OOCCH_3$		123–125					434	440	65.97; 66.47	6.25; 6.17	12.54; 12.76	—	66.33	6.03	12.91	—

organosilicon compounds with phenylene-carbon and phenylene-siloxane units

$$—Si — A — Si \quad \langle\ \rangle \quad — Si — A — Si—, \quad \text{where } A = —O— \text{ or } —CH_2—,$$

and diacetoxyparaphenylenedisilanes—for the preparation of polysilphenylenes with functional groups.

Experimental Part

1,4-Bis-(diethylbromosilyl)-benzene. To a solution of 50 g (0.2 mole) of 1,4-bis-(diethylsilyl)-benzene in 120 ml of CCl_4 there was added, over 4 hr, 64 g (0.4 mole) of bromine dissolved in 100 ml of CCl_4, with cooling and vigorous stirring. The temperature of the cooling bath was maintained within the range 0-(−5°). After the entire amount of bromine had been added, the reaction mixture was purged for 2 hr with a stream of dry nitrogen to remove hydrogen bromide.

There was obtained 49.8 g (yield 61.2%) of 1,4-bis-(diethylbromosilyl)-benzene. B.p. 175–178°/2 mm; d_4^{20} 1.3224; n_D^{20} 1.5440; MR_D: found 97.53; calculated 97.03. Mol. wt.: found 415; 417; calculated 408.3.

Found %: Br 39.21, 39.30
$C_{14}H_{24}Si_2Br_2$. Calculated %: Br 39.21

A fraction with b.p. 79–85°/20 mm was also isolated in an amount of 12.5 g (12.2%), representing unpurified diethyldibromosilane. Mol. wt.: found 261; 265; calculated 246.0.

Found %: Br 63.30, 63.45
$C_4H_{10}SiBr_2$. Calculated %: Br 65.04

1,4-Bis-(methylphenylbromosilyl)-benzene. The bromination was carried out under conditions analogous to those used for preparing 1,4-bis-(diethylbromosilyl)-benzene. The reaction employed: 63.6 g (0.2 mole) of 1,4-bis-(methylphenylsilyl)-benzene, 64 g (0.4 mole) of bromine, and 250 ml of CCl_4.

There was obtained 49.2 g (yield 52.0%) of 1,4-bis-(methylphenylbromosilyl)-benzene. B.p. 248–250°/3 mm; m.p. 61–62°; mol. wt.: found 480; 486; calculated 476.3.

Found %: Br 33.20, 33.30
$C_{20}H_{20}Si_2Br_2$. Calculated %: Br 33.61

On distillation the following fractions were also isolated: 103–110°/7 mm (11.2 g); 110–230°/7 mm (10.5 g) and 230–262°/7 mm (12.3 g).

The first fraction (yield 7.3%), according to analysis for percentage bromine content (found %: Br 55.45; 55.36; calculated %: Br 57.76) and molecular weight (mol. wt.: found 302; 306; calculated 280.2), represents unpurified methylphenylbromosilane.

1,4-Bis-(diphenylsilyl)-benzene. To the organomagnesium compound prepared from 20 g (0.8 g-atom) of magnesium in absolute tetrahydrofuran and 75.5 g (0.32 mole) of *p*-dibromobenzene dissolved in 150 ml of absolute tetrahydrofuran, 152 g (0.69 mole) of diphenylchlorosilane was added. The reaction mixture was heated for 2 hr at 64–65°. The magnesium salt was then separated, the tetrahydrofuran and the fraction up to 200°/1 mm Hg were distilled off. The residue with b.p. above 200°/1 mm Hg, which crystallized on standing, was dissolved in chloroform and precipitated with methanol. After two further recrystallizations from benzene, 75.8 g (yield 52.3%) of 1,4-bis-(diphenylsilyl)-benzene was obtained. M.p. 83°. Mol. wt.: found 434; 442; calculated 442.3. H(active): found % 0.460; 0.472; calculated 0.456.

Found %: C 81.11, 81.43; H 6.07, 6.05; Si 12.97, 12.83
$C_{30}H_{26}Si_2$. Calculated %: C 81.44; H 5.91; Si 12.66

1,4-Bis-(diphenylbromosilyl)-benzene. Bromination was carried out under conditions analogous to the preparation of 1,4-bis-(diethylbromosilyl)-benzene. The reaction was charged with 13.3 g (0.03 mole) of 1,4-bis-(diphenylsilyl)-benzene in 150 ml of CCl_4 and 9.6 g (0.06 mole) of bromine in 30 ml of CCl_4. After the entire amount of bromine had been added and the mixture had stood for 4 hr, yellowish crystals precipitated, which were recrystallized from CCl_4. 5.7 g (yield 31.5%) of 1,4-bis-(diphenylbromosilyl)-benzene was obtained. M.p. 197–198°. Molecular weight: found 573; 587; calculated 600.4.

Found, %: C 60.23; 60.33; H 4.17, 3.89; Si 9.20, 9.10; Br 25.60, 25.50
$C_{30}H_{24}Si_2Br_2$. Calculated, %: C 60.00; H 4.00; Si 9.34; Br 26.60

1,4-Bis-(diethylacetoxysilyl)-benzene. 25 g (0.1 mole) of 1,4-bis-(diethylsilyl)-benzene, dissolved in 180 ml of absolute diethyl ether, and 40.8 g (0.4 mole) of acetic anhydride in the presence of 1 g of zinc chloride were heated for 3 hr at the boiling point of ether and then for about 1 hr at 60° after removal of the ether. Heating was stopped after the temperature of the reaction mixture had spontaneously risen to 110°. The cooled mixture was filtered, and the filtrate was distilled in vacuo.

21.5 g (yield 59.6%) of 1,4-bis-(diethylacetoxysilyl)-benzene was obtained. B.p. 174.5–175°/3 mm; d_4^{20} 1.0310; n_D^{20} 1.4938. MR_D: found 103.45; calculated 102.35. Molecular weight: found 366; 368; calculated 366.5.

Found, %: C 58.94, 58.90; H 8.18, 8.18; Si 15.26, 15.15
$C_{18}H_{30}Si_2O_4$. Calculated, %: C 58.98; H 8.25; Si 15.31

1,4-Bis-(methylphenylacetoxysilyl)-benzene. A mixture consisting of 31.8 g (0.91 mole) of 1,4-bis-(methylphenylsilyl)-benzene, 40.8 g (0.4 mole) of acetic anhydride, and 200 ml of absolute diethyl ether in the presence of 1 g of zinc chloride was heated for 2.5 hr at the boiling point of ether. Then the reaction mixture, from which ether and light fractions up to 65° had been distilled off, was filtered, and the filtrate was heated at 70–73° until the temperature of the reaction mixture spontaneously rose to 125°. On standing, yellowish crystals precipitated from the mixture. After threefold recrystallization from decalin and drying, 26.5 g (yield 61.0%) of 1,4-bis-(methylphenylacetoxysilyl)-benzene was obtained.

M.p. 123–125°. Molecular weight: found 434; 440; calculated 434.6.

Found, %:	C 65.97, 66.17;	H 6.25, 6.17;	Si 12.54, 12.76
$C_{24}H_{26}Si_2O_4$. Calculated, %:	C 66.33;	H 6.03;	Si 12.91

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