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SHORT COMMUNICATION

Arylenedisilanols

In connection with our recent interest in condensation polymers from arylenedisilanols and silazanes or siloxazanes, we have extended the synthetic methods originally reported for the preparation of arylenebis(dialkoxysilanes)[1,2] to a number of arylenebis(alkoxysilanes) as intermediates for the arylenedisilanols. Difunctional organometallic reagent (sodium or magnesium), formed in the presence of organoalkoxychlorisilanes, afforded arylenedisilane derivatives as the product of a single synthesis step. Considerable work has been reported on the use of this "*in situ*" procedure when the silane employed in the method is a diorganochlorosilane[3,4,5], but the method has also been shown to be effective with a diorganodichlorosilane[6], a diorganodialkoxysilane[1,7], and an organotrialkoxysilane[8]. The *in situ* procedure for the preparation of functional arylenedisilanes appears to be applicable to a number of combinations of reactants.

Silanol intermediates prepared in the present work from various difunctional organosilanes are reported in Table 1. Compounds (II), (III), and (VI) were prepared by adding mixtures of *m*- or *p*-dibromobenzene and the required chloroalkoxysilane in tetrahydrofuran to magnesium. Compounds (VIII) and (IX) were similarly prepared, but in the condensation of the chloroalkoxysilanes with bis(*p*-bromophenyl) ether, sodium was used rather than magnesium. Compound (I) could not be satisfactorily prepared from the chloroalkoxysilane, but was readily obtained when the preformed difunctional Grignard reagent was treated with dimethyldiethoxysilane[9]. Concomitant addition of reactants to magnesium was also employed for the preparation of (IV), (V), and (VII) in which mixtures of *m*- or *p*-dibromobenzene and chlorodiphenylsilane in tetrahydrofuran or dichloromethylphenylsilane in ether were used. Since Compound (V) could not be crystallized and decomposed during distillation, the crude product was used directly in the preparation of the silanol.

Conversion of the intermediates to silanols was effected by Merker and Scott's method[5], and the properties of the silanols are reported in Table 2. The procedure was somewhat simplified when arylenebis(alkoxysilanes) were used since the conversion of the silicon hydrides to the alkoxysilanes was unnecessary. Traces of recrystallization solvents were extremely difficult to remove from several of the silanols, particularly (XII) and (XVI), and extensive drying in a vacuum oven was necessary. However, no evidence could be found for the formation of stoichiometric complexes. Considerable difficulty was encountered in removing trace impurities from (XII) by recrystallization. Correct analyses for elements were obtained in products in different preparations melting at 216–217° and at 224–226°, but products melting at intermediate temperatures were also obtained. The infrared and NMR spectra of the low and high melting compounds did not differ.

Beck and Chaffee[3] reported that attempts to prepare *p*-phenylenebis(methylphenylsilanol) produced siloxanes rather than the silanol. Indeed, an amorphous solid was obtained when *p*-phenylenebis(ethoxymethylphenylsilane) was hydrolyzed, but after four days' storage, the solid crystallized. The product was a mixture of silanol

TABLE 1

XRR'SiZSiRR'X

Compound No.	*X*	*R*	*R'*	*Z*	*B.p.* [°C (*mm*)]	n_D^{20}	*Yield* (%)	*Analyses calcd./found*[a] (%)		
								C	*H*	*Si*
(I)	OC_2H_5	CH_3	CH_3	p-C_6H_4	119–120 (3.6)[b]	1.4782	38			
(II)	OC_2H_5	CH_3	CH_3	m-C_6H_4	93–95 (0.5)	1.4757	40	59.51 59.27	9.28 9.08	19.88 19.55
(III)	OC_2H_5	C_6H_5	C_6H_5	p-C_6H_4	m.p. 158–161[c,d,e]		28			
(IV)	H	C_6H_5	C_6H_5	p-C_6H_4	m.p. 102–105[f,g]		39	81.39 81.37	5.92 6.00	12.69 12.74
(V)	H	C_6H_5	C_6H_5	m-C_6H_4			63			
(VI)	OC_2H_5	CH_3	C_6H_5	p-C_6H_4	187–188 (0.06)	1.5541	53	70.88 70.81	7.44 7.43	
(VII)	Cl	CH_3	C_6H_5	m-C_6H_4	179–185 (0.07)		21	62.00 61.97	5.20 5.17	14.50 14.33
(VIII)	OC_2H_5	CH_3	CH_3	p,p'-$C_6H_4OC_6H_4$	141–142 (0.1)	1.5213[h]	56	64.12 63.92	8.07 8.10	15.00 15.03
(IX)	OC_2H_5	CH_3	C_6H_5	p,p-$C_6H_4OC_6H_4$	226–243 (0.04)	1.5783	41	72.24 72.01	6.87 6.71	11.26 11.11

[a] Analyses by Spang Microanalytical Laboratory, Ann Arbor Michigan. [b] Reported[1], b.p. 127–128° (3.5 mm), n_D^{25} 1.4752. [c] M.p.'s are all capillary, uncorrected. [d] Reported[13], 158–160°. [e] From toluene. [f] Reported[3], 107–108°. [g] From petroleum ether, b.p. 60–90°. [h] Reported[7], 1.5176 (25°).

TABLE 2

HORR'SiZSiRR'OH

Compound				*M.p.*	*Yield*	*Analyses calcd./found*		
No.	*R*	*R'*	*Z*	(°*C*)	(%)	*C*	*H*	*Si*
(X)	CH_3	CH_3	p-C_6H_4	136–137[a,b]	60			
(XI)	CH_3	CH_3	m-C_6H_4	79–81[c,d]	64	53.04	8.01	24.81
						53.11	7.89	24.70
(XII)	C_6H_5	C_6H_5	p-C_6H_4	224–226[b]	78	75.90	5.52	11.84
						76.19	5.76	11.77
				216–217[b]		76.19	5.82	11.58
(XIII)	C_6H_5	C_6H_5	m-C_6H_4	111–113[b]	27[e]	75.90	5.52	11.84
						76.99	5.78	11.31
(XIV)	CH_3	C_6H_5	p-C_6H_4	128–140	80	68.52	6.33	16.03
						68.36	6.23	16.09
				128–129[f]				
				156–158[f]		68.38	6.53	15.96
(XV)	CH_3	C_6H_5	m-C_6H_4	101–102	23	68.52	6.33	16.02
						68.72	6.26	15.93
				139–140	20	68.47	6.23	15.96
(XVI)	CH_3	CH_3	p,p'-$C_6H_4OC_6H_4$	103–104[g]	89	60.33	6.96	17.64
						60.09	6.88	17.50
(XVII)	CH_3	C_6H_5	p,p'-$C_6H_4OC_6H_4$	48–55	51	70.54	5.92	12.69
						70.73	6.09	12.51

[a] Reported[14], 138–139°. [b] From toluene. [c] Reported[3], 82–83°. [d] From benzene. [e] Yield from p-$C_6H_4Br_2$. [f] From petroleum ether/toluene. [g] Reported[3,7], 96°, 85–91°.

stereoisomers, which could be separated by fractional crystallization. A similar pair of isomers was obtained in the preparation of *m*-phenylenebis(methylphenylsilanol). Except in the 700–800 cm^{-1} region, the pairs of isomers had similar infrared spectra and their NMR spectra were superimposable.

The infrared spectra of the compounds reported in Tables 1 and 2 were consistent with their structure and showed no unusual features. NMR spectra of representative compounds are reported in Table 3.

Experimental

Chlorodiphenylsilane[10], b.p. 115–122° (1.5–2.0 mm), chloroethoxymethylphenylsilane[11], b.p. 111–112° (28–30 mm), and chlorodimethylethoxysilane[12], b.p. 93–95° were used in the experiments.

Chlorodiphenylethoxysilane. After a mixture of 25.3 g (0.55 mole) of anhydrous ethanol and 43.5 g (0.55 mole) of pyridine was added to a solution of 139 g (0.55 mole) of dichlorodiphenylsilane, the mixture was stirred 30 min, filtered, and fractionally distilled. Chlorodiphenylethoxysilane (116 g, 81 %) boiled at 117° (0.7 mm). (Found: C, 63.91; H, 5.80; Cl, 13.70. $C_{14}H_{15}ClOSi$ calcd.: C, 63.98; H, 5.75; Cl, 13.49%.)

P-Phenylenebis(ethoxymethylphenylsilane). The following procedure is typical of the Grignard method for preparing intermediates. To 10.9 g (0.45 g-atom) of previously activated magnesium turnings covered with 40 ml of tetrahydrofuran was added a mixture of 47.2 g (0.2 mole) of *p*-dibromobenzene, 90.0 g (0.45 mole) of

TABLE 3

PROTON CHEMICAL SHIFTS OF ARYLENEDISILANES

No.	$\tau(C_6H_4Si)$	$\tau(C_6H_4O)$	$\tau(SiOH)$	$\tau(CH_2C)$	$\tau(CH_3C)$	$\tau(CH_3Si)$	$\tau(SiH)$
(I)[a]	2.39			6.32 quad. *J* 7 cps	8.85 trip. *J* 7 cps	9.66	
(IV)[a]	2.32–2.73 mult.						4.52
(VIII)[b]	2.76 doub. *J* 8 cps	3.30 doub. *J* 7 cps		6.62 quad. *J* 7 cps	9.14 trip. *J* 7 cps	9.94	
(X)[c]	2.34		4.12			9.67	
(XII)[c]	2.40–2.83 mult.		2.99				
(XIII)[c]	2.20–2.57 mult.		2.68				
(XIV)[c]	2.80–3.24 mult.		3.58			9.60	
(XV)[c]	2.19–2.58 mult.		3.42			9.35	
(XVI)[c]	2.31 doub. *J* 7 cps	2.92 doub. *J* 6 cps	4.09			9.67	

[a] In carbon tetrachloride. [b] Neat liquid. [c] In dimethyl sulfoxide.

chloroethoxymethylphenylsilane, and 100 ml of tetrahydrofuran over a 1.5-h period. After the mixture was refluxed for 3 h, cooled, treated with 100 ml of petroleum ether to precipitate the magnesium salts, and filtered, fractional distillation on a spinning band column gave 43.0 g (53%) of *p*-phenylenebis(ethoxymethylphenylsilane).

Bis(p-dimethylethoxysilylphenyl) ether. The following procedure is typical of the sodium method for preparing intermediates. A mixture of 43.0 g (0.13 mole) of bis(*p*-bromophenyl) ether, 39.0 g (0.28 mole) of chlorodimethylethoxysilane, and 13.0 g (0.56 g-atom) of 1-mm diameter sodium wire in 500 ml of ether was allowed to reflux and, after the reaction became sufficiently slow, the mixture was heated to maintain reflux and stirred for a total of 24 h. When the mixture was cooled, filtered, and fractionally distilled, 27.4 g (56%) of bis(*p*-dimethylethoxysilylphenyl) ether was obtained.

m-Phenylenebis(dimethylsilanol). The following is a typical procedure for converting the ethoxy intermediates to silanols. A solution of 21.4 g (0.076 mole) of *m*-phenylenebis(dimethylethoxysilane) in 75 ml of dry ethanol was added slowly to a stirred solution of 15.2 g (0.38 mole) of sodium hydroxide in 10 ml of water and 80 ml of methanol. A solution of 15.2 g of sodium hydroxide in 45 ml of water was added in 10 min and the mixture was stored 1 h. After the mixture was poured slowly into 200 ml of water and 500 g of ice containing 110 g (0.81 mole) of potassium dihydrogen phosphate, the diol was collected by filtration and recrystallized from benzene.

m-Phenylenebis(chloromethylphenylsilane) was hydrolyzed in ether with an equivalent quantity of aqueous sodium hydroxide.

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