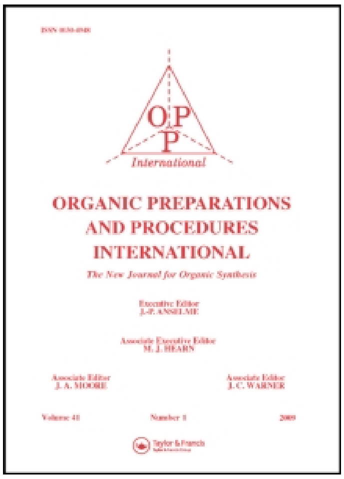

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SYNTHESIS OF *p*-BIS (DIMETHYLHYDROXYSILYL) BENZENE

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gave the chloromethyl acid (197 mg.; 90%), which was recrystallized from acetonitrile, mp. 200-201.5°, lit.[1] 178-179°); IR (KBr); 1695 cm^{-1} (CO_2H); 60 MHz NMR (DMSO-d_6): δ2.23, 2.33, 2.37, s, CH_3; 4.78, s, CH_2; 6.97, s, arom. H.

Anal. Calcd. for $C_{11}H_{13}ClO_2$: C, 62.1; H, 6.1; Cl, 16.7.
Found: C, 62.4; H, 6.4; Cl, 16.6.

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SYNTHESIS OF p-BIS(DIMETHYLHYDROXYSILYL)BENZENE

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p-Bis(dimethylhydroxysilyl)benzene is a convenient precursor for the synthesis of poly(tetramethyl-p-silphenylene-polysiloxane),[1] reported to be more stable than polydimethylsiloxane both to atmospheric oxidation and degradation at elevated temperatures.[2] However, methods involving Grignard reagents are not suitable for the large-scale preparation of this very important compound. For example, the bis(silyl)benzene is generally prepared from *p*-bis(dimethylchlorosilyl)benzene or *p*-bis(dimethylethoxysilyl)benzene obtained from the *in situ* Grignard reaction of *p*-dibromobenzene with dimethyldichlorosilane[3] or dimethyldiethoxysilane,[4] but the yield of each intermediate is at best 25% and 40%, respectively. More recently, the Grignard reaction of *p*-dibromobenzene with flammable and expensive dimethylchlorosilane was reported to give 66-88% yields of *p*-bis(dimethylhydrosilyl)benzene which can be converted to the bis(dimethylhydroxysilyl)benzene by hydrolysis.[2,5]

We report herein an alternative method which does not use the Grignard reaction thus providing a convenient large-scale synthesis of *p*-bis(dimethylhydroxysilyl)benzene.

$$p\text{-BrC}_6\text{H}_4\text{Br} + 2\text{ClMe}_2\text{SiSiMe}_2\text{Cl} \xrightarrow[-2\text{Me}_2\text{SiClX}]{\text{Pd(PPh}_3)_4} p\text{-XMe}_2\text{SiC}_6\text{H}_4\text{SiMe}_2\text{X}$$

$$\xrightarrow[\text{MeOH}]{\text{Na}} \xrightarrow[\text{H}_2\text{O}]{\text{NaOH}} p\text{-HOMe}_2\text{SiC}_6\text{H}_4\text{SiMe}_2\text{OH} \qquad (\text{X} = \text{Br or Cl})$$

The reaction of 1,2-dichloro-1,1,2,2-tetramethyldisilane[6] with *p*-dibromobenzene proceeded smoothly at reflux in the presence of 0.35 mol% (based on the dibromobenzene charged) of tetrakis(triphenylphosphine)palladium(0)[7] to give *p*-bis(dimethylhalosilyl)benzenes in excellent yield. Subsequent hydrolysis of the halosilylbenzenes gave *p*-bis(dimethylhydroxysilyl)benzene in 76% overall yield.

EXPERIMENTAL

IR spectra were recorded on a Hitachi EPI-3G spectrophotometer. NMR spectra were taken on a Varian EM-360 instrument with TMS as an internal standard. Mass spectra were recorded on a JEOL JMS-07 spectrometer. GLC analyses were carried out with Ohkura 802T instrument, using Teflon columns (50-100 X 0.4 cm) packed with Silicone SE-30 and DCQF-1 on Celite 545 (60/80). Mps. are uncorrected. 1,2-Dichloro-1,1,2,2-tetramethyldisilane[6] and tetrakis(triphenylphosphine)palladium(0)[8] were prepared according to literature directions. Other reagents were commercially available and used without further purification.

<u>*p*-Bis(dimethylhalosilyl)benzenes</u>.- In a 200 ml flask equipped with a fractional distillation column were placed *p*-dibromobenzene (46.2 g, 0.20 mol), 1,2-dichloro-1,1,2,2-tetramethyldisilane (112, g, 0.60 mol), tetrakis(triphenylphosphine)palladium(0) (0.80 g, 0.0007 mol) and mesitylene (80 ml). The flask was well flushed with nitrogen and heated to reflux with stirring for 40 hrs. while the resulting dimethylchlorosilanes (e.g., dimethyldichlorosilane and dimethylbromochlorosilane) were distilled from the reaction zone. The resulting residue was then diluted with pentane (300 ml) and the precipitated catalyst was filtered. Evaporation of the filtrate under reduced pressure gave 65 g of brownish white solid. The GLC chromatogram of the solid showed two peaks (approximately 1:1) and a small sample of each component was isolated by GLC. The NMR and mass spectra of the first compound eluted (white solid) was quite consistent with the structure of *p*-bis(dimethyl-

chlorosilyl)benzene.

^{1}H NMR (CCl_4): δ 0.64 (s, 12H, $SiMe_2Cl$), 7.60 (s, 4H, phenyl).

Mass (relative intensities of isotope peaks in molecular ions):

m/e 262 (9.0), 264 (6.0), 266 (1.4). Calcd for $C_{10}H_{16}Si_2Cl_2$: m/e 262 (9.0), 264 (6.0), 266 (1.0).

The second peak was found by NMR and mass analyses to be a mixture of 1-(dimethylbromosilyl)-4-(dimethylchlorosilyl)benzene and p-bis(dimethylbromosilyl)benzene.

^{1}H NMR (CCl_4): δ 0.64 (s, 3.7H, $SiMe_2Cl$), 0.78 (s, 8.3H, $SiMe_2$-Br), 7.53 (m, 4H, phenyl).

Mass (relative intensities of isotope peaks in molecular ions):

m/e 306 (6.0), 308 (8.0), 310 (2.6). Calcd for $C_{10}H_{16}Si_2BrCl$: m/e 306 (6.0), 308 (8.0), 310 (2.0).

m/e 350 (1.0), 352 (2.0), 354 (1.1). Calcd for $C_{10}H_{16}Si_2Br_2$: m/e 350 (1.0), 352 (2.0), 354 (1.0).

p-Bis(dimethylhydroxysilyl)benzene.-[5] The ethereal solution of the crude p-bis(dimethylhalosilyl)benzenes (65 g) obtained above was added dropwise to absolute methanol (70 ml) pretreated with 11 g of sodium. The mixture was added with vigorous stirring to a mixture of sodium hydroxide (35 g), methanol (210 ml) and water (21 ml). The resulting mixture was allowed to stand for 15 min to which was added a solution of sodium hydroxide (35 g) in water (210 ml). After standing for 1 hr. with occasional stirring, this mixture was poured into a vigorously stirred solution of potassium dihydrogen phosphate (310 g) in excess ice and water. The resulting precipitate was filtered, washed with water (twice), and dried in vacuo to give 34 g (76% yield based on p-dibromobenzene) as light, white needles, mp. 134-134.5°, lit.[5] 136.5-137°.

IR (KBr disk): 3450-3000 (s, OH), 1430 (s, SiPh), 1255 (s, SiMe), 1140 cm^{-1} (s, SiPh).

^1H NMR (acetone-d_6): δ 0.35 (s, 12H, $SiMe_2OH$), 5.06 (s, 2H, OH), 7.71 (s, 4H, phenyl).

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THE SYNTHESIS OF 3-R-7-CARBOMETHOXYMETHYLENE-7H-1,2,4-TRIAZOLO[3,4-b]-1,3,4-THIADIAZIN-6-ONES

Submitted by (2/11/80)

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The vicinal amino and mercapto groups of 4-amino-3-mercapto-(4H)-1,2,4-triazoles (Ia-d) constitute useful bridging loci for fusion of hetero rings onto the *s*-triazole. Fused