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Palladium/Hydrogen Catalyzed Alcoholysis of Benzylsilanes

Colin G. Pitt,* Alan E. Friedman, Douglas H. Rector,
and Mansukh C. Wani*

Chemistry and Life Sciences Division
Research Triangle Institute
P.O. Box 12194
Research Triangle Park, North Carolina 27709

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Summary: Certain benzylsilanes are converted to methoxy or ethoxysilanes and toluene when treated with methanol or ethanol in the presence of hydrogen and catalytic amounts of palladium on charcoal. The reaction is promoted by a Si-phenyl substituent and probably proceeds by a S_NSi displacement mechanism.

The benzyl-silicon bond is generally considered to be rather inert. It is stable to heat, acids, many oxidizing and reducing agents, and is only cleaved by relatively strong nucleophiles [1]. It is therefore of interest to find that certain benzylsilanes may be converted to alkoxysilanes at room temperature by stirring an alcoholic solution under a hydrogen atmosphere in the presence of a catalytic amount of palladium on charcoal.

Four examples are shown in Scheme 1. Compounds I-III were converted to the methoxy or ethoxysilanes within 24–40 hr. Benzylcyclohexyldimethylsilane(IV) reacted more slowly, and only 10% cyclohexyldimethylmethoxysilane was formed after 9 days. m-Trifluoromethylbenzylcyclohexyldimethylsilane was even less reactive than IV, despite the fact that a m-CF_3 substituent is known to enhance the rate of nucleophilic cleavage of the Si-benzyl bond by a factor of 100 [2].

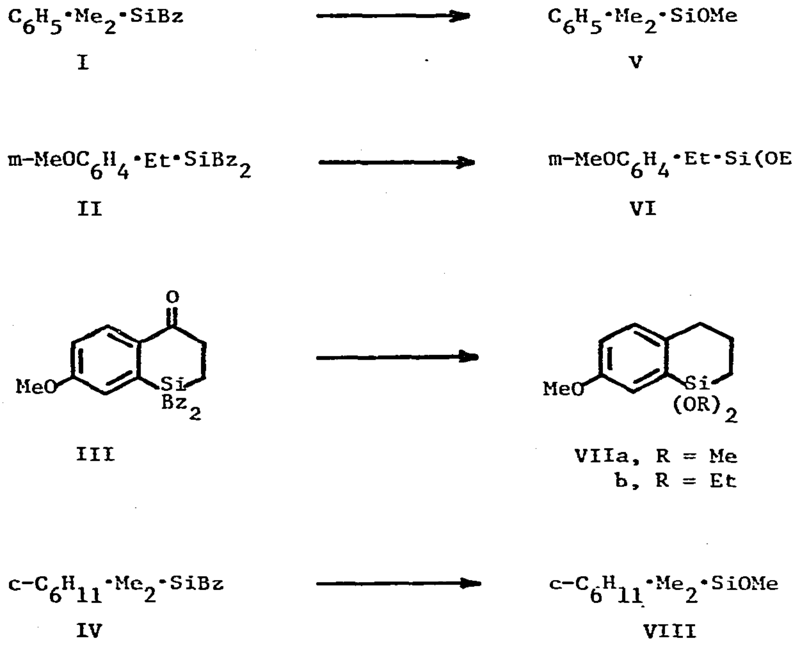
No hydrogen was consumed during the reaction, although no cleavage occurred in its absence. The cleaved benzyl group(s) was recovered as toluene. Cleavage did not occur in the hindered alcohol, tert-butanol, or in acetic acid, or in aprotic solvents such as benzene, ethyl acetate, carbon tetrachloride, and acetonitrile. No cleavage of the benzyl groups of 3-(dibenzyl-m-methoxyphenylsilyl)propan-1-ol occurred in <u>benzene</u>, despite the possibility of intramolecular alcoholysis. Platinum on carbon was not an effective catalyst.

The conversion of benzylsilanes to alkoxysilanes under the above conditions could conceivably occur by hydrogenolysis, followed by palladium catalyzed alcoholysis [3] of the resulting Si–H bond (Eq 1). However, this would not explain the ineffectiveness of acetic acid as a solvent. We tentatively suggest that the mechanism involves complexation

$$\begin{gathered} R_3SiBz + Pd(O) \rightarrow R_3SiPdBz \xrightarrow{H_2} R_3SiH + BzH + Pd(O) \\ R_3SiH + R'OH \longrightarrow R_3SiOR' + H_2 \end{gathered} \tag{1}$$

of the benzyl π-system with the palladium surface, generating a good leaving group, followed by S_N^-Si displacement of "Bz-Pd" by the alcohol. Hydrogen would then serve to reduce "Bz-Pd" to toluene and regenerate palladium. Such a mechanism is consistent with the lack of reaction in aprotic solvents, in tert-butanol (steric), and in acetic acid (poor nucleophile), and could also explain the rate enhancing effect of a phenyl substituent [1,4] (c f. I–III vs. IV). However, the failure of m-trifluoromethylbenzylcyclohexyldimethylsilane to undergo rapid cleavage would suggest that complexation of the Pd catalyst with the benzyl-π system, rather than Si–C cleavage, is the rate determining step. Whatever the process, it appears to differ from and complements the catalytic cleavage of (Si)-aryl groups by platinum(II) and palladium (II) derivatives [5].

We have already pointed out the potential of Si-benzyl as a protecting group in the synthesis of functionalized organosilicon compounds [6]. The silatetralin VII is an example of a functionalized organosilane which could not be synthesized with comparable simplicity by any other route.



$C_6H_5 \cdot Me_2 \cdot SiBz \longrightarrow C_6H_5 \cdot Me_2 \cdot SiOMe$

I → V

$m\text{-}MeOC_6H_4 \cdot Et \cdot SiBz_2 \longrightarrow m\text{-}MeOC_6H_4 \cdot Et \cdot Si(OEt)_2$

II → VI

III → VIIa, R = Me
b, R = Et

$c\text{-}C_6H_{11} \cdot Me_2 \cdot SiBz \longrightarrow c\text{-}C_6H_{11} \cdot Me_2 \cdot SiOMe$

IV → VIII

Scheme 1

Experimental

IR spectra were measured with a Perkin-Elmer 267 Spectrophotometer. NMR spectra were recorded on a Varian Model A-100 spectrometer, using tetramethylsilane (TMS) or methylene chloride as an internal standard; chemical shifts are expressed in δ units. Mass spectra were determined using an Associated Electrical Industries MS-902 instrument. Gas liquid chromatographic analysis was carried out using a Varian Model 1400 instrument with a column containing 3% SE-30 on Variport. All cleavage reactions were followed by GLC. No products other than toluene and alkoxysilane were detected.

Dibenzylethyl-m-methoxyphenylsilane(II). Ethylene was bubbled through dibenzyl-m-methoxyphenylsilane [6] (3.0 g) and chloroplatinic acid (0.02 ml, 0.1N in isopropanol) for 5 hr at room temperature. Distillation gave II (2.9 g, 85%), b.p. 190°-200°/0.01 mmHg. IR (liquid film): ν (C=C) 1600 m, 1540 s, 1490 s. ^{1}H-NMR ($CDCl_3$): δ 0.88 (m, 5, SiC_2H_5), 2.36 [s, 4, $Si(\underline{CH_2}C_6H_5)_2$], 3.68 (s, 3, OCH_3), 6.82-7.30 (m, 14, ArH). Exact mass: 346.175 (calcd. for $C_{23}H_{26}SiO$: 346.175). (Found: C, 79.62; H, 7.68. Calcd.: C, 79.72; H, 7.56).

Benzylcyclohexyldimethylsilane(IV). A stirred mixture of cyclohexene (1.68 g, 20.5 mmol), benzyldimethylsilane [7] (1.00 g, 7.04 mmol) and chloroplatinic acid (0.02 ml, 0.1N in isopropanol) was heated at 75° for 22 hr (absence of Si-H absorption in IR spectrum). Distillation gave IV (0.879 g, 54%), b.p. 85-87°/0.25 mm Hg. IR (liquid film): ν (C=C) 1610 m, 1500 s cm^{-1}. NMR ($CDCl_3$): δ 0.00 (s, 6, $SiMe_2$), 1.10-1.77 (m, 11, cyclohexyl protons), 2.07 (s, 2, $\underline{CH_2}C_6H_5$), 6.87-7.23 (m, 5, ArH). Exact mass: 232.165 (calcd. for $C_{15}H_{24}Si$: 232.165). (Found: C, 77.11; H, 10.39. Calcd.: C, 77.51; H, 10.41).

1,1,7-Trimethoxy-1-silatetralin(VIIa). A solution of 4,4-dibenzyl-6-methoxy-4-sila-1-tetralone [6] (III, 5.0 g) in methanol (100 ml) was added to a prehydrogenated suspension of 10% palladium on carbon (0.5 g) in the same solvent (500 ml) under H_2 and stirred for 40 hr. Filtration and distillation gave VIIa (1.71 g, 54%), b.p. 97-99°/0.75 mmHg. IR (liquid film): ν (Si-OMe) 2840 s, ν (C=C) 1600 m, 1560 m, ν (Si-O) 1060 s (br) cm^{-1}. NMR ($CDCl_3$): δ 0.98 (t, 2, J=6Hz, C-2), 1.98 (m, 2, C-3), 2.73 (t, 2, J=6Hz, C-4), 3.56 [s, 6, $Si(OCH_3)_2$], 3.80 (s, 3, OCH_3), 6.80-7.12 (m, 3, ArH). Exact mass: 238.102 (calcd. for $C_{12}H_{18}SiO_3$: 238.102). (Found: C, 60.40; H, 7.47. Calcd.: C, 60.47; H, 7.61).

<u>1,1-Diethoxy-7-methoxy-1-silatetralin(VIIb)</u>. When the above procedure was repeated using ethanol as a solvent, VIIb was obtained in 50% yield, b.p. 94-98°/0.05 mmHg. IR (liquid film): ν (Si-OEt) 2860 m, ν (C=C) 1600 m, 1520 m, ν (Si-O) 1060 s (br) cm^{1}. NMR ($CDCl_3$): δ 0.96 (t, 2, J=6Hz, C-2), 1.20 (t, 6, J=6Hz, $CH_2C\underline{H}_3$), 2.0 (m, 2, C-3), 2.72 (t, 2, J=6Hz, C-4), 3.78 (s, 3, OCH_3), 3.82 (q, 4, J=6Hz, $C\underline{H}_2CH_3$), 6.78-7.12 (m, 3, ArH). Exact mass: 266.133 (calcd. for $C_{14}H_{22}SiO_3$: 266.134). (Found: C, 62.97; H, 8.01. Calcd.: C, 63.12; H, 8.32).

<u>Diethoxyethyl-m-methoxyphenylsilane(VI)</u>. A suspension of II and the catalyst was stirred under H_2 for 24 hr using the same conditions as for the preparation of VIIb. Filtration and distillation gave VI (83%), b.p. 80-85°/0.04 mmHg. IR (CCl_4): ν (C=C) 1540 m, ν (Si-O) 1100 s, 1060 s cm^{1}. NMR ($CDCl_3$): δ 0.90 (m, 5, $SiC_2\underline{H}_5$), 1.21 [t, 6, J=6Hz, $Si(OCH_2C\underline{H}_3)_2$], 3.78 (s, 3, OCH_3). 3.82 [q, 4, J=6Hz, $Si(OC\underline{H}_2CH_3)_2$], 6.86-7.36 (m, 4, ArH). Exact mass: 254.133 (calcd. for $C_{13}H_{22}SiO_3$: 254.133). (Found: C, 61.13; H, 8.93. Calcd.: C, 61.38; H, 8.72).

<u>Dimethylmethoxyphenylsilane(V)</u>. [8] A suspension of benzyldimethylphenylsilane [9] (I) and the catalyst was stirred under H_2 for 24 hr using the same conditions as for the preparation of VIIa. Filtration and distillation gave V (67%), b.p. 92-95°/17 mmHg. IR (liquid film) ν (SiOMe) 2840 s, ν (C=C) 1580 w, ν (Si-O) 1050 s (br) cm^{-1}. NMR ($CDCl_3$):

δ 0.48 [s, 6, $Si(CH_3)_2$], 3.0 (s, 3, OCH_3), 6.77-7.17 (m, 5, ArH).

The solvent recovered from distillation (b.p. 65°) of the reaction mixture was diluted with water and the upper phase was identified as toluene (84%) by its ^{1}H-NMR spectrum and GLC. In all other experiments the formation of toluene was established by GLC.

Cyclohexyldimethylmethoxysilane(VIII). A suspension of IV and the catalyst was stirred under H_2 for 9 days using the same conditions as for the preparation of VIIa. GLC of the reaction mixture indicated that only 10% of IV had been consumed. The product was identified by GLC-MS. Mass: 172 (calcd. for $C_9H_{20}SiO$: 172).

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