

CONVERSION OF DISILANES TO FUNCTIONAL MONOSILANES

II *. PREPARATION OF SOME NITROPHENYLTRIMETHYLSILANES BY TETRAKIS(TRIPHENYLPHOSPHINE)PALLADIUM(0) CATALYZED REACTIONS OF HEXAMETHYLDISILANE WITH NITROHALOBENZENES

HIDEYUKI MATSUMOTO, KAZUO YOSHIHIRO, SHIGERU NAGASHIMA, HAMA O WATANABE and YOICHIRO NAGAI

Department of Chemistry, Gunma University, Kiryu, Gunma 376 (Japan)

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Summary

o-, *m*- and *p*-Nitrophenyltrimethylsilanes and 2,4-dinitrophenyltrimethylsilane were conveniently prepared by the reactions of hexamethyldisilane with the corresponding nitrohalobenzenes catalyzed by tetrakis(triphenylphosphine)-palladium(0).

Introduction

Few satisfactory methods have been available for the preparation of nitrophenyltrimethylsilanes [2]. The previously studied nitration of phenyltrimethylsilane with an appropriate nitrating agent was accompanied by nitro- and proto-desilylations and was characterized by a lack of regioselectivity. For example, Benkeser and Brumfield reported that nitration of phenyltrimethylsilane with copper nitrate in acetic anhydride gave a 30/40/30 mixture of *o*-, *m*- and *p*-nitrophenyltrimethylsilanes in 65% combined yield, along with 25% nitrobenzene [3]. The nitration with 90% fuming nitric acid led to the formation of the *ortho*-, *meta*- and *para*-nitroisomers in a ratio of 26.6/41.7/31.6 at 0–10°C. This process also was accompanied by the formation of some nitrobenzene [4]. On the other hand, nitration of *p*-bis(trimethylsilyl)benzene with nitric acid in acetic anhydride at reflux gave an 82% yield of *p*-nitrophenyltrimethylsilane via nitrodesilylation [5]. However, it should be stressed that explosions sometimes have been observed during reactions of this type [6]. Therefore, it seemed of importance to explore an alternate method for making

* For part I see ref. 1.

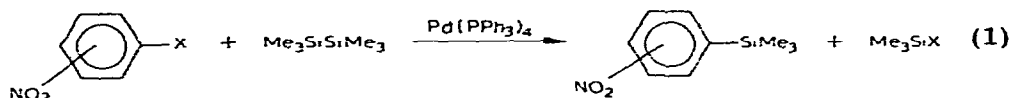
nitrophenyltrimethylsilanes which is free of such disadvantages.

We have recently reported that cleavage reaction of disilanes with halobenzenes such as bromobenzene and chlorobenzene proceeded smoothly to give arylsilanes in good yields under the catalytic influence of tetrakis(triphenylphosphine)palladium(0) [1].

We report here the preparation of some nitrophenyltrimethylsilanes by means of this reaction which has proved to be a convenient route to these compounds.

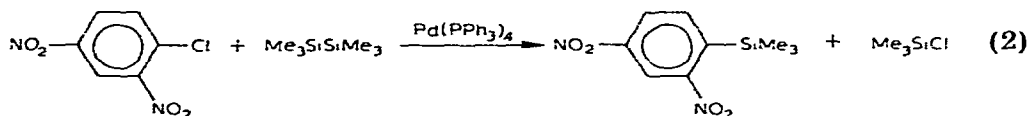
Results and discussion

The synthesis of *o*-, *m*- and *p*-nitrophenyltrimethylsilanes and 2,4-dinitrophenyltrimethylsilane from hexamethyldisilane and the corresponding nitrohalobenzenes was investigated (eq. 1 and 2).



X = Cl : *o*-, *m*- and *p*-nitro-isomers

X = Br : *m*-nitro-isomer



Our preliminary experiments [1] showed that in the Si-Si cleavage reaction introduction of an electron-withdrawing substituent, e.g., the nitro group, increased the reactivity of the chlorobenzene, in line with the known ability of such a group to promote oxidative addition reactions with tetrakis(triphenylphosphine)palladium(0) [7].

Although the reaction could be carried out by refluxing a xylene solution of hexamethyldisilane, a nitrochlorobenzene and the palladium(0) complex, slow rates were occasionally encountered. However, these reactions proceeded satisfactorily in sealed tubes at 150–160°. The reaction with 1–2.3 mol% (based on the nitrochlorobenzene charged) of the palladium(0) complex generally required 40 hours or more to reach completion and produced essentially a 1/1 mixture of the desired nitrophenyltrimethylsilane and trimethylchlorosilane which was easily resolved by distillation. The catalyst could be removed from the resulting mixture by addition of petroleum ether. The product yields were good (60–85%, see Table 1).

m-Nitrophenyltrimethylsilane was also prepared using the corresponding nitro-bromobenzene. The reaction was faster than with *m*-nitrochlorobenzene and was complete within 30 hours. The yield of the nitrophenyltrimethylsilane, however, was only 35% based on the nitrochlorobenzene charged and a considerable amount of tar was produced as well.

TABLE 1

REACTIONS OF HEXAMETHYLDISILANE WITH SOME NITROHALOBENZENES IN THE PRESENCE OF TETRAKIS(TRIPHENYLPHOSPHINE)PALLADIUM(0)^a

Nitrohalobenzene	Conditions	Nitrophenyl-trimethylsilane obtained	Yield (%) ^d
<i>o</i> -NO ₂ C ₆ H ₄ Cl	150°C, 40 h ^c	<i>o</i> -NO ₂ C ₆ H ₄ SiMe ₃	83 (65)
<i>m</i> -NO ₂ C ₆ H ₄ Cl ^b	160°C, 48 h ^c	<i>m</i> -NO ₂ C ₆ H ₄ SiMe ₃	85 (53)
<i>m</i> -NO ₂ C ₆ H ₄ Br	reflux, 28 h	<i>m</i> -NO ₂ C ₆ H ₄ SiMe ₃	60 (35)
<i>p</i> -NO ₂ C ₆ H ₄ Cl	160°C, 40 h ^c	<i>p</i> -NO ₂ C ₆ H ₄ SiMe ₃	86 (61)
2,4-(NO ₂) ₂ C ₆ H ₃ Cl	160°C, 44 h ^c	2,4-(NO ₂) ₂ C ₆ H ₃ SiMe ₃	85 (51)

^a Reactions were carried out in xylene with a 1/1.8–2.5 mixture of a nitrohalobenzene and the disilane, the catalyst concentration being about 1 mol% based on the nitrohalobenzene charged unless otherwise indicated. ^b The catalyst concentration was 2.3 mol%. ^c Carried out in a sealed Pyrex tube. ^d Yields (via GLC) are based on the nitrohalobenzene charged. In the parentheses are given isolated yields. Conversion of the nitrohalobenzene charged was complete.

Although recent investigation by Tsui et al. has shown that aryl nitro compounds were reduced by disilanes (including hexamethyldisilane) at high temperatures [8], we have not found that such reactions occur in the present system as indicated by the absence of a significant amount of hexamethyldisiloxane as the oxidation product.

We conclude that tetrakis(triphenylphosphine)palladium(0)-catalyzed cleavage reactions of hexamethyldisilane with mononitrochlorobenzenes or dinitrochlorobenzene provide a convenient synthesis of nitrophenyltrimethylsilanes which has the advantages of simplicity of the reaction procedure, accessibility of the starting materials and catalyst, reasonable yields of the products and potentially wider applicability.

Experimental

Boiling points and melting points are uncorrected. IR spectra were recorded with a Hitachi EPI-3G instrument. NMR spectra were recorded with a Varian A-60D instrument. Mass spectra were recorded on a Hitachi RMU-7D mass spectrometer. GLC analyses were carried out with an Ohkura Model 802 gas chromatograph fitted with 100–150 × 0.4 cm. Teflon column containing 20% DCQF-1, 25% Silicone KF-96, 20% SE-30 and 20% XF-1105 on 60/80 mesh Chromosorb W.

Reagent grade *o*-, *m*- and *p*-nitrochlorobenzenes, 2,4-dinitrochlorobenzene and *m*-nitrochlorobenzene were used without further purification. Hexamethyldisilane [9] and tetrakis(triphenylphosphine)palladium(0) [10] were prepared according to literature methods.

Preparation of nitrophenyltrimethylsilanes from nitrochlorobenzenes and hexamethyldisilane

o-Nitrochlorobenzene (4.37 g, 30 mmol), the disilane (8.78 g, 60 mmol), tetrakis(triphenylphosphine)palladium(0) (0.35 g, 0.30 mmol) and xylene (15 ml) were introduced into a Pyrex tube containing a Teflon-covered stirring-bar.

TABLE 2
CHARACTERIZATION OF THE NITROPHENYLTRIMETHYLSILANES

Nitrophenyltri- methylsilane	IR (cm ⁻¹) ^a	NMR (δ, ppm) ^b	Mass (m/e) (Rel. intensity) ^c
<i>o</i> -NO ₂ C ₆ H ₄ SiMe ₃	1606 (C=C), 1530 (NO ₂), 1430 (Si-Phenyl), 1350 (NO ₂), 1255 (Si-Me), 1115 (Si-Phenyl), 850 (Si-Me), 790, 750 (Si-Me), 736	0.37 (s, 9H, Si-CH ₃), 7.39-8.23 (m, 4H, aromatic H)	196 (M ⁺ , 6) 180 (M ⁺ - Me, 100)
<i>m</i> -NO ₂ C ₆ H ₄ SiMe ₃	1603 (C=C), 1530 (NO ₂), 1425 (Si-Phenyl), 1355 (NO ₂), 1255 (Si-Me), 1115 (Si-Phenyl), 850 (Si-Me), 785, 760 745 (Si-Me), 680	0.36 (s, 9H, Si-CH ₃), 7.32-8.40 (m, 4H, aromatic H)	195 (M ⁺ , 17) 180 (M ⁺ - Me, 100)
<i>p</i> -NO ₂ C ₆ H ₄ SiMe ₃	1610 (C=C), 1530 (NO ₂), 1430 (Si-Phenyl) 1355 (NO ₂), 1260 (Si-Me), 1120 (Si-Phenyl), 850 (Si-Me), 835, 745 (Si-Me)	0.35 (s, 9H, Si-CH ₃) 7.67 (d, 2H, J 9 Hz, aromatic H), 8.13 (d, 2H, J 9 Hz, aromatic H)	195 (M ⁺ , 4) 180 (M ⁺ - Me, 100)
2,4-(NO ₂) ₂ C ₆ H ₃ SiMe ₃ ^d	1600 (C=C), 1530 (NO ₂), 1420 (Si-Phenyl), 1350 (NO ₂), 1250 Si-Me), 1100 (Si-Phenyl), 920, 850 Si-Me), 835, 745 (Si-Me)	0.42 (s, 9H, Si-CH ₃) 8.03 (d, 1H, J 9 Hz, aromatic H), 8.50 (dd, 1H, J 2 and 9 Hz, aromatic H), 8.93 (d, 1H, J 2 Hz, aromatic H)	240 (M ⁺ , 6) 215 (M ⁺ - Me, 100)

^a Neat (*o*-NO₂C₆H₄SiMe₃ and *m*-NO₂C₆H₄SiMe₃): KBr disk (*p*-NO₂C₆H₄SiMe₃ and 2,4-(NO₂)₂C₆H₃SiMe₃). ^b CCl₄ solution with Me₄Si. ^c 70 eV. The detailed cracking patterns of the mononitrophenyltrimethylsilanes have already been presented [11]. ^d Satisfactory analytical data was reported for this compound.

The tube was cooled in liquid nitrogen, evacuated to 0.3 mmHg, sealed and heated at 150°C for 40 hours with stirring. The tube was then cooled to room temperature and opened. GLC analysis of the resulting mixture indicated that the nitrochlorobenzene had been completely consumed and that the nitrophenyltrimethylsilane had been produced in 83% yield based on the nitrochlorobenzene charged. The mixture was diluted with petroleum ether (30–60°C) to precipitate the catalyst which was removed by filtration. Evaporation of the filtrate under reduced pressure and subsequent distillation of the residue gave 3.81 g (65% yield) of *o*-nitrophenyltrimethylsilane as a yellow liquid, b.p. 115–117°C; n_D^{20} 1.5325 (lit. [3] b.p. 117°C (10 mmHg); n_D^{20} 1.5321). Spectral data are presented in Table 2.

A similar reaction gave *m*-nitrophenyltrimethylsilane (85% yield) as a yellow liquid, b.p. 124–125°C (10 mmHg); n_D^{20} 1.5342 (lit. [3] b.p. 126°C (10 mmHg); n_D^{20} 1.5239). Spectral data are given in Table 2. *p*-Nitrophenyltrimethylsilane also was prepared by this method in 61% yield, b.p. 127–128°C (10 mmHg); m.p. 38.0–38.8°C (lit. [3] b.p. 129°C (10 mmHg); m.p. 38–39°C).

This procedure also served in the preparation of 2,4-dinitrophenyltrimethylsilane in 85% yield by GLC. Distillation gave 7.32 g (51% yield) as yellow crystals, b.p. 140–141°C. (4 mmHg); m.p. 56–58°C. The structure of the product was confirmed by spectral data (Table 2) and elemental analysis. Found: C, 45.65; H, 5.08; N, 11.79. $C_9H_{12}N_2O_4Si$ calcd.: C, 44.98; H, 5.04; N, 11.66%.

Preparation of m-nitrophenyltrimethylsilane from m-nitrochlorobromobenzene and hexamethyldisilane

A mixture of the nitrochlorobromobenzene (10.1 g, 50.0 mmol), the disilane (14.7 g, 100 mmol), the palladium(0) complex (0.29 g, 0.25 mmol) and xylene (15 ml) was refluxed under nitrogen for 28 hours with stirring. The resulting mixture was diluted with petroleum ether (45 ml) and the dark precipitate was removed by filtration. Evaporation of the filtrate and distillation of the residue gave 3.40 g (35% yield) of *m*-nitrophenyltrimethylsilane, b.p. 123–124.5°C (10 mmHg).

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