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## A Convenient Method for the Protodesilylation of Aryltrimethylsilanes

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Abstract: A mild and highly effective procedure for the removal of aromatic trimethylsilyl groups involving treatment of ArSiMe<sub>3</sub> with Me<sub>3</sub>SiCl, KI and H<sub>2</sub>O in acetonitrile, is reported.

The protodesilylation of aryl silanes is of importance both as a model for aromatic substitution reactions<sup>1</sup> and e.g. for the unblocking of protected reactive aromatic positions, for isotopic labeling and for a number of other synthetic applications.<sup>2-4</sup> The most frequently used reagents include CF<sub>3</sub>COOH<sup>2</sup> and CsF<sup>3</sup> or Bu<sub>4</sub>NF<sup>4</sup> for acid-sensitive substrates. The fluoride-based reactions often require heating and prolonged reaction times and we required a fast, mild and reliable method for the desilylation of some ketal-protected tetrahydroxybenzenes, e.g. **1a**. We now report that protodesilylation proceeds smoothly and rapidly at room temperature upon treatment of ArSiMe<sub>3</sub> with equivalent amounts of KI, Me<sub>3</sub>SiCl and H<sub>2</sub>O in CH<sub>3</sub>CN. In the case of **1a**, no deketalization occurred and **1b** could be isolated in almost quantitative yield. The method has been used for selective cleavage of an Ar-Si-bond in the presence of an Ar-O-Si-bond and in some other cases as summarized in Table 1.



In a typical experiment equimolar amounts of 1a, KI and  $H_2O$  in dry acetonitrile were treated with a stoichiometric amount of Me<sub>3</sub>SiCl for 15 minutes, followed by conventional work-up to give 1b in 97 % isolated yield.<sup>5</sup> Replacement of the reactants with an equimolar amount of HI in CH<sub>3</sub>CN resulted in complete consumption of 1a, but only a *ca*. 30% yield of the desilylated product 1b as determined by GLC. Using identical reaction conditions the TBDMS-protected phenol 2 was cleanly desilylated in 91% isolated yield; ca. 3% of Me<sub>3</sub>Si-Ar-OH was present in the crude reaction mixture as determined by GLC. Replacing H<sub>2</sub>O with D<sub>2</sub>O gave the deuterodesilylated product with an isotopic purity of >98% in 93% isolated yield.<sup>6</sup>

The reaction proceeds very fast with electron-rich substrates; 2-trimethylsilyl-1,3,5-trimethoxybenzene (3) was quantitatively desilylated within one minute whereas 1-trimethylsilylnaphthalene (4) required ca. 20 minutes reaction time. Unactivated substrates are not well suited for the present method; i.e. 4-chlorotrimethyl-silylbenzene (5) required a 5-fold excess of the desilylating mixture, prolonged reaction time and heating in order to achieve a high degree of conversion, but this invariably led to significant by-product formation.



Treatment of 4 as above but in the absence of KI for 30 min resulted in the formation of 2 % of naphthalene as determined by GLC. Replacement of Me<sub>3</sub>SiCl with CH<sub>3</sub>COCl resulted in 2 % and 15 %, respectively, yield of naphthalene after 30 min in the absence and presence of KI; in the latter case 7 % of an unidentified compound also was formed. Finally we note that the method appears not to be useful for 1,3-dioxolanes; when the ketal 6 was treated as described above both deketalization and desilylation was observed, but no significant amounts of the desired protodesilylated ketal-protected compound could be detected.

Substrate	Equivalents desilylating mixture	Temp, °C	Time, h	Isolated yield, %
1a	1.0	20	0.25	97
2	1.0	20	0.25	91
3	1.0	20	0.10	96
4	1.1	20	0.50	95
5	5.0	60	5.0	70a

Table 1. Protodesilylation of Aryltrimethylsilanes with Me<sub>3</sub>SiCl, KI and H<sub>2</sub>O in Acetonitrile.

a) Determined by GLC.

## **References and notes**

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- 5. In a typical experiment 2.0 mmol of, respectively, the aryl silane, KI and H<sub>2</sub>O were stirred in 30 ml of dry acetonitrile and 2.0 mmol of trimethylsilyl chloride was added in one portion. After stirring for 15 min the mixture was poured onto aq. NaHCO<sub>3</sub>/ether, dried, evaporated and filtered through a short pad of Silica with heptane:ether 20:1 to give the essentially pure desilylated product after evaporation.
- 6. CH<sub>3</sub>CN (Anhydroscan, <0.02% H<sub>2</sub>O) was dried over MgSO<sub>4</sub>, passed through a column packed with neutral alumina and treated with CaH<sub>2</sub>. 0.5 % D<sub>2</sub>O (v/v) was added and the drying procedure was repeated. After two repetitions, the solvent was used for deuterodesilylations as described above, replacing H<sub>2</sub>O with D<sub>2</sub>O. The isotopic purity was determined in the case of 1a to be >99% D by mass spectroscopy (APcI). In the case of 2 mass spectroscopy provided unreliable results, but the deuterium content was estimated by NMR to be >98%.

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