

## Preparation of Aryl- and Heteroaryltrimethylsilanes

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This review presents a comprehensive survey of the synthetic methods for aryl- and heteroaryltrimethylsilanes. Their preparation can result from direct silicon-carbon coupling reactions, from cycloaddition reactions, or through modification of silylaromatic or -heteroaromatic compounds by incorporation of further functional groups or by conversion of substituents already present.

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### 1. Introduction

The use of silicon in organic synthesis is enjoying a growing popularity due to its various preparative advantages<sup>1</sup>. The trimethylsilyl group is an especially good example in that it has long been applied as a protective group in the chemistry of peptides, carbohydrates, and many other compounds, which can be easily removed. Moreover, it has advantageous effects on the volatility, stability, and solubility of compounds so protected<sup>1</sup>. On the other hand, the specific reaction of silylated compounds with electrophiles (e.g. alkylating or acylating agents) has been only recently systematically investigated. The reactions of trimethylsilyl enol ethers<sup>2</sup> are of special interest, because different regio- and stereoselectivity relations can occur than are encountered in the reactions of metal enolates. One class of compounds,

whose mode of reaction towards electrophiles is especially interesting, is the aryl- and heteroaryltrimethylsilanes. Since reactivity and selectivity of C-H and C-SiR<sub>3</sub> bonds differ significantly, isomers that are difficult to obtain by conventional electrophilic aromatic substitution (normally deprotonation reactions) can, in some cases, be more conveniently prepared by desilylation reactions<sup>3</sup>.



deprotonation reaction



desilylation reaction

If desilylation reactions are to be of wide preparative importance in the chemistry of aromatic compounds, a simple access to the corresponding aryl- and heteroaryltrimethylsilanes is necessary. Apart from an older Japanese paper<sup>4</sup>, no review of the preparation of this class of compounds exists. One finds reference to the preparation of arylsilanes<sup>5,6,7</sup> only in connection with general publications on organosilicon compounds.

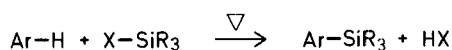
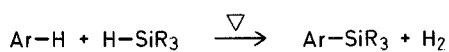
We intend to give a survey of *C*-trimethylsilylated aromatic and heteroaromatic compounds. The literature through 1977 has been reviewed. Compounds which carry, besides the trimethylsilyl group, other group IV substituents (e.g. R<sub>3</sub>Sn) are not included, since they undergo electrophilic reactions<sup>8</sup> at the position bearing the substituent more easily than aryltrimethylsilanes<sup>3</sup>.

## 2. Direct Introduction of Trimethylsilyl Groups into Aromatic and Heteroaromatic Compounds

In principle, trimethylsilyl groups can be introduced into aromatic or heteroaromatic compounds in a radical, nucleophilic, or electrophilic manner.

### 2.1. Radical Silylation of Aromatic and Heteroaromatic Compounds

The silylation of aromatic compounds via free radical processes can be induced thermally, photochemically, or by other radical sources. Aromatic compounds react with silicon hydrides in the gas phase at 500–850<sup>9</sup>, in the liquid phase under autogeneous pressure at 350–500<sup>9</sup>, and in the presence of peroxides at 135<sup>10</sup>; gas phase condensations<sup>11</sup> and reactions via electrical discharge<sup>12</sup> have also been reported with silicon halides.



The reactions of aryl halides with silicon hydrides in the gas phase at 500–700<sup>13</sup> and in the liquid phase at 350–450<sup>8</sup> also afford arylsilanes. Disilanes that can be thermally split into silyl radicals react in the same way<sup>14</sup>. All these reactions are of high energy

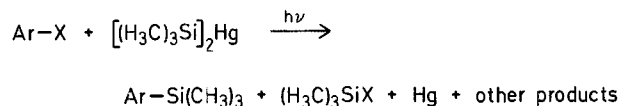
consumption, give mixtures of products, and thus have limited laboratory use. Their usefulness is further reduced because the yield of arylsilanes decreases with increasing number of methyl groups in the SiX<sub>3</sub>-residue. Since the reactants are readily obtainable, however, these methods of preparation may be of industrial importance.

Silyl radicals can also be obtained radiochemically (e.g.  $\gamma^{15}$ ,  $e^{16}$ ) and show, in principle, the same mode of reaction with aromatic compounds as those induced thermally. U.V.-Irradiation of aryl halides in the presence of trimethylsilane produces aryltrimethylsilanes along with other products in various yields, e.g. phenyltrimethylsilane (11%)<sup>17</sup> or pentafluorophenyltrimethylsilane (53%)<sup>18</sup>.

#### Pentafluorophenyltrimethylsilane<sup>18</sup>:

Hexafluorobenzene (8.6 g, 0.1 mol) and trimethylsilane (7.4 g, 0.1 mol) are irradiated (U.V. light) with shaking for 240 h in a 300 ml silica tube. The tube is cooled to –196° prior to opening. Trimethylfluorosilane is separated by fractional condensation and the remaining liquid is distilled to give *hexafluorobenzene*; yield: 9.1 g (49%); b.p. 80–82° and *pentafluorophenyltrimethylsilane*; yield: 6.5 g (53% based on hexafluorobenzene consumed); b.p. 170°.

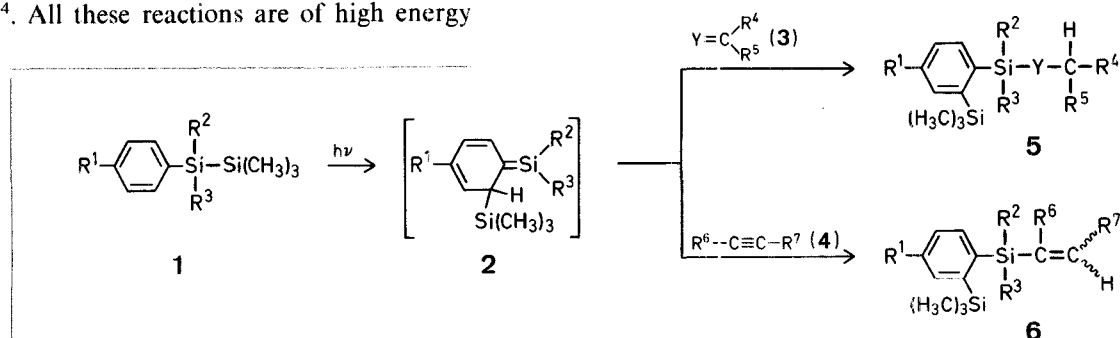
Aryltrimethylsilanes are also produced by the U.V. photolysis of bis[trimethylsilyl]mercury in aromatic compounds as solvents, though usually only in moderate yields<sup>19,20,21</sup>.



X = H, F

In the photolysis of substituted disilanes **1** [R<sup>1</sup> = H, CH<sub>3</sub>, *t*-C<sub>4</sub>H<sub>9</sub>; R<sup>2</sup>, R<sup>3</sup> = H, CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>, Si(CH<sub>3</sub>)<sub>3</sub>], reactive intermediates **2** are formed by a [1,3]sigmatropic rearrangement. In the presence of trapping agents such as **3** [Y = CH<sub>2</sub>, O; R<sup>4</sup> = H, CH<sub>3</sub>, *t*-C<sub>4</sub>H<sub>9</sub>; R<sup>5</sup> = CH<sub>3</sub>, Si(CH<sub>3</sub>)<sub>3</sub>,  $\cdot\text{C}(\text{CH}_3)\text{---CH}_2$ , etc.] or **4** [R<sup>6</sup> = H, Si(CH<sub>3</sub>)<sub>3</sub>; R<sup>7</sup> = H, *t*-C<sub>4</sub>H<sub>9</sub>, Si(CH<sub>3</sub>)<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>], intermediate **2** undergoes addition reactions to give the aryltrimethylsilanes **5** or **6**, respectively<sup>22</sup>.

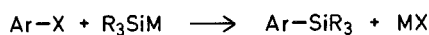
In contrast, photolysis of **1** in the presence of dimethyl sulfoxide takes a different pathway. Here, the



products are found to be disiloxanes, arylsilanes [among these are aryltrimethylsilanes (56–57%)], dimethylsilanone, and dimethyl sulfide<sup>23</sup>.

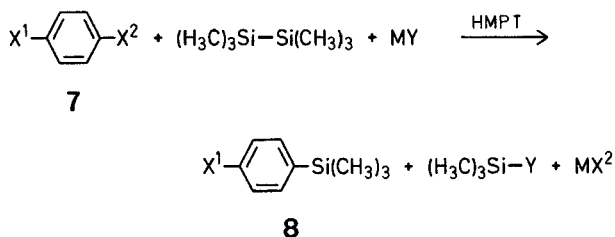
## 2.2. Nucleophilic Silylation of Aromatic and Heteroaromatic Compounds

The reaction of triorganosilylmetal compounds<sup>24</sup> with aryl and heteroaryl halides leads to triorganosilylaromatic compounds.



M = Li, Na, K

The preparative value of this reaction using isolated trimethylsilyllithium<sup>25</sup>, -sodium<sup>25</sup>, and -potassium<sup>25</sup> is limited, due to the instability of these compounds and to the possibility of a metal/halide exchange (formation of disilanes). This method has gained significance only through the *in situ* formation of the silylating agents from hexamethyldisilane with appropriate bases. The reaction of aryl halides **7** with the disilane in this way gives aryltrimethylsilanes **8** in yields of 63–92%<sup>26</sup>.

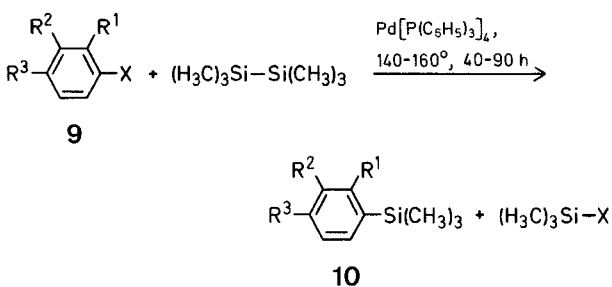


X<sup>1</sup> = H<sub>3</sub>C, Cl

X<sup>2</sup> = Cl, Br, J

MY = LiCH<sub>3</sub>, NaOCH<sub>3</sub>, KOCH<sub>3</sub>

2-Pyridyltrimethylsilane is similarly obtained from 2-bromopyridine, the disilane, and potassium methoxide in 80% yield<sup>26</sup>. The exact mechanism is still uncertain, although an aryne pathway can be excluded because of the distribution of isomers obtained. Cleavage of hexamethyldisilane with aryl halides **9** under the catalytic influence of tetrakis[triphenylphosphine]palladium(0) affords similar products **10**. This reaction is especially important for the preparation of nitrophenyltrimethylsilanes, since the nitro function is destroyed by all other silylating methods (Table 1).



**Table 1.** Aryltrimethylsilanes **10** via Palladium-Catalyzed Cleavage of Hexamethyldisilane with Aryl Halides **9**

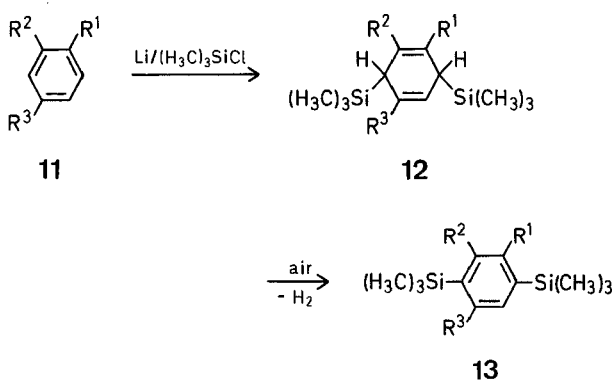
| Substrate <b>9</b><br>No. | X  | R <sup>1</sup>   | R <sup>2</sup>   | R <sup>3</sup>    | Yield [%]<br>of <b>10</b> | Reference |
|---------------------------|----|------------------|------------------|-------------------|---------------------------|-----------|
| a                         | Cl | H                | H                | H                 | 98                        | 27        |
| b                         | Br | H                | H                | H                 | 99                        | 27        |
| c                         | Br | H                | H                | H <sub>3</sub> CO | 39                        | 27        |
| d                         | Cl | H                | H                | O <sub>2</sub> N  | 61–100                    | 27, 28    |
| e                         | Cl | H                | O <sub>2</sub> N | H                 | 53                        | 28        |
| f                         | Br | H                | O <sub>2</sub> N | H                 | 35                        | 28        |
| g                         | Cl | O <sub>2</sub> N | H                | H                 | 65                        | 28        |
| h                         | Cl | O <sub>2</sub> N | H                | O <sub>2</sub> N  | 40–51                     | 28, 29    |

### 2-Nitrophenyltrimethylsilane (**10g**)<sup>28</sup>:

A mixture of 2-nitrochlorobenzene (4.37 g, 30 mmol), hexamethyldisilane (8.78 g, 0 mmol), tetrakis[triphenylphosphine]palladium(0) (0.35 g, 0.3 mmol), and xylene (15 ml) is heated in a pyrex tube at 150° for 40 h with stirring. The mixture is diluted with petroleum ether to precipitate the catalyst, which is removed by filtration. Evaporation of the filtrate and subsequent distillation gives **10g**; yield: 7.81 g (65%); b.p. 115–117°/10 torr; n<sub>D</sub><sup>20</sup>: 1.5325.

Aryl iodides form stable adducts with the palladium catalyst and therefore will not react in this way<sup>27</sup>. Reaction of hexamethyldisilane with dihalobenzenes produces halophenyltrimethylsilanes and bis[trimethylsilyl]benzenes<sup>30,31</sup>.

The reductive silylation of aromatic compounds is also an example of the nucleophilic-type reaction. It differs from the reactions of aryl halides discussed above because of the lack of an anionic leaving group. Consequently, cyclohexadiene derivatives **11** are formed by an addition reaction from aromatic compounds **11**. They rearomatize in a subsequent elimination step often achieved by the introduction of air (Table 2) to **13**. Even without introduction of air, smaller<sup>32,35</sup> or larger<sup>35,36</sup> amounts of **13** are formed together with the adducts **12**, depending on the reaction conditions.



### 1,4-Bis[trimethylsilyl]benzene (**13a**) from Benzene<sup>35</sup>:

Method A: Indirect: Benzene (1 mol), finely cut lithium (3 mol), chlorotrimethylsilane (4 mol), and tetrahydrofuran (250 ml) are stirred for 12 days at room temperature in an inert atmosphere. After the mixture has been filtered and volatile products removed in vacuum, product **12a** (60%), contaminated with about 5% **13a**, crystallizes. The product mixture in carbon tetrachloride is well stirred during the introduction of air to yield **13a** quantitatively.

Method B: Direct: Performed as above except with immediate introduction of air after which **13a** is isolated by distillation and recrystallization; yield: 65%, m.p. 98°.

**Table 2.** Reductive Silylation of Arenes **11** with Lithium/Chlorotrimethylsilane<sup>a</sup> in Tetrahydrofuran to **12** and Subsequent Air Oxidation<sup>b</sup> to **13**<sup>34,35</sup>

| Substrate <b>11</b><br>No. | R <sup>1</sup>                          | R <sup>2</sup>   | R <sup>3</sup>   | Yield [%]<br>of <b>12</b> <sup>c</sup> |
|----------------------------|---|------------------|------------------|--|
| a                          | H                                       | H                | H                | 60–85                                  |
| b                          | H <sub>3</sub> C                        | H                | H                | 67                                     |
| c                          | H <sub>3</sub> C                        | H <sub>3</sub> C | H                | 30                                     |
| d                          | H                                       | H <sub>3</sub> C | H <sub>3</sub> C | 75–80                                  |
| e                          | H <sub>3</sub> C                        | H                | H <sub>3</sub> C | 70–75                                  |
| f                          | H <sub>3</sub> C                        | H <sub>3</sub> C | H <sub>3</sub> C | 5                                      |
| g                          | <i>i</i> -C <sub>3</sub> H <sub>7</sub> | H                | H                | 50                                     |

<sup>a</sup> Use of magnesium/chlorotrimethylsilane in hexamethylphosphoric triamide results in lower (10–25%) yields of **12**<sup>35,37</sup>.

<sup>b</sup> Only papers which include this rearomatization step are listed.

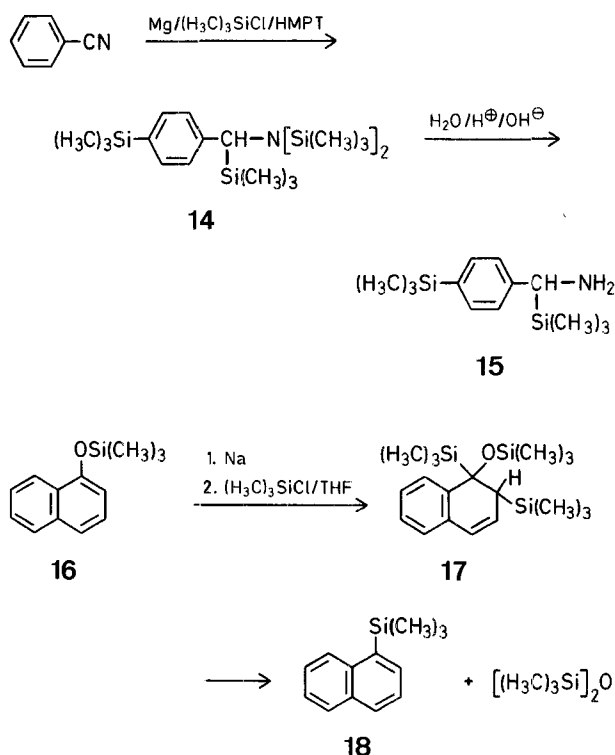
<sup>c</sup> Yield of **12**→**13** almost quantitative in each case.

Naphthalenes and anthracenes do not react with metals and chlorotrimethylsilane as specifically and usually give poorer yields than the benzene derivatives **11**<sup>33,38,39,40</sup>.

Besides the 1,4- and 1,2-adducts<sup>38</sup>, monosilylated adducts<sup>40</sup> are formed; also, the rearomatization step often requires special conditions<sup>39–42</sup>. Despite the above mentioned disadvantages, reductive silylation is the best known method for the preparation of some sensitive compounds (e.g. trimethylsilylanthracenes). Biphenyl reacts with an excess of sodium/chlorotrimethylsilane to form a complex mixture of silylated isomers<sup>43</sup>.

It has been demonstrated, by investigations dealing with the mechanism of reductive silylation, that sequences of radical anion intermediates and not dianions are involved<sup>32,38</sup>. The reaction of chlorotrimethylsilane with highly activated magnesium in tetrahydrofuran at –10° to give trimethylsilane or hexamethyldisilane is assumed to be proof of the existence of organosilyl Grignard compounds<sup>44</sup>. The general mode of reaction of the system metal/chlorotrimethylsilane/donor solvent with various functional groups has been reviewed<sup>45</sup>. Under the conditions of reductive silylation, reactions of aromatic aldehydes, ketones, esters, imines, and nitriles lead to product mixtures that can be derived from radical anion sequences<sup>45</sup>. Thus, from reaction of benzonitrile, the tetrakis[trimethylsilyl] compound **14** is obtained which, upon the hydrolytic work-up, affords the benzylamine **15** (64%)<sup>46</sup>.

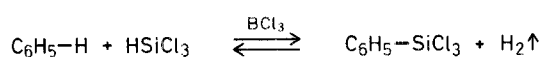
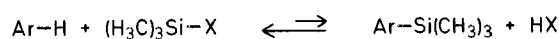
A variant of the reductive silylation, which affords better yields and homogeneous product formation, especially with naphthalenes, requires the use of 1-trimethylsilyloxynaphthalene (**16**). The primarily formed adduct **17** rearomatizes to **18** with the elimination of hexamethyldisiloxane<sup>47</sup>.



Special conditions have been found with *o*-methoxyaryloxazolines that permit the cleavage of the methoxy group, in proximity to a potential carboxylic acid function, with trimethylsilyllithium or the corresponding Grignard compound by nucleophilic substitution of the methoxy group<sup>48</sup>. The addition of alkyl lithium compounds to styrenes and subsequent treatment with chlorotrimethylsilane affords alkylphenyltrimethylsilanes (18–85%)<sup>49</sup>.

### 2.3. Electrophilic Silylation of Aromatic and Heteroaromatic Compounds

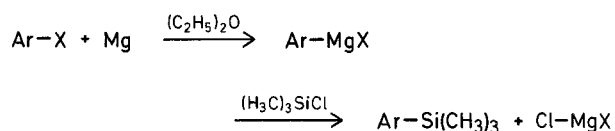
The direct introduction of silyl groups into aromatic compounds via a normal electrophilic substitution has not yet been achieved. Even such reactive substrates as phloroglucine trimethyl ether or 1,3,5-tripyrrolidinobenzene<sup>50</sup> have not afforded *C*-silylation<sup>51</sup> with either chlorotrimethylsilane or the even more reactive trimethylsilyl trifluoromethanesulfonate<sup>52</sup>. Not even by addition of Friedel Crafts catalysts can this reaction be effected<sup>53</sup>. The instability of silylenium ions [R<sub>3</sub>Si<sup>+</sup>]<sup>54,55,56</sup> may be one reason for this behaviour, but the very easily occurring reverse reaction [protodesilylation, which can be used for the simple preparation of compounds of the type (CH<sub>3</sub>)<sub>3</sub>Si–X]<sup>57</sup>, is more decisive. When the reverse reaction is excluded (for instance by the irreversible removal of hydrogen) direct silylation of aromatic compounds with boron trichloride as catalyst occurs<sup>58</sup>.

















Despite this fact, electrophilic introduction of silyl groups into aromatic and heteroaromatic compounds is the most important preparative method for this class of compounds. However, instead of the aromatic compounds, their considerably more nucleophilic organometallic derivatives are usually allowed to react with chlorotrimethylsilane or similar silylating agents.

### 2.3.1. Preparations via Organomagnesium Compounds

Many aryltrimethylsilanes have been prepared by conventional Grignard reactions [i.e. defined formation of the Grignard compound and subsequent silylation (Table 3)]. The use of cyanotrimethylsilane or ethoxytrimethylsilane<sup>60</sup> instead of chlorotrimethylsilane are exceptions.



**Table 3.** Aryltrimethylsilanes via Conventional Grignard Reactions

| Ar-X  | Yield [%] | Reference  |
|---|-----------|------------|
|  | 41-92     | 72-77      |
|  | 76        | 77         |
|  | 60        | 78         |
|  | 41        | 70         |
|  | 50        | 61         |
|  | 80        | 61, 72, 76 |
|  | 56        | 61, 79     |
|  | —         | 80         |
|  | —         | 80         |
|  | 78        | 81         |
|  | 80        | 81         |
|  | 71        | 81         |
|  | 84        | 81         |
|  | 76        | 82         |

**Table 3.** Continued

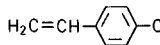
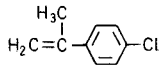
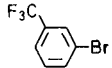
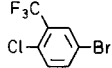
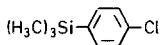
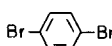
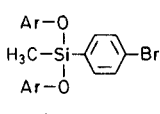
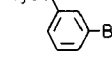
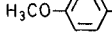
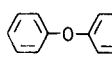
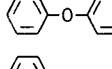
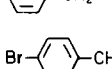
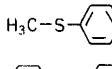
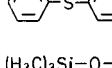
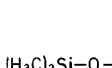
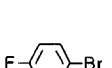
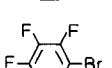
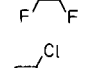
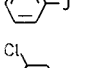
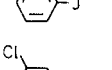
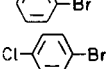
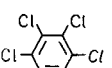
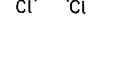




| Ar-X  | Yield [%]               | Reference                             |
|---|-------------------------|---------------------------------------|
|    | 70                      | 65, 81 <sup>a</sup> , 83 <sup>a</sup> |
|    | 71                      | 84 <sup>a</sup>                       |
|    | 65                      | 85, 86                                |
|    | —                       | 86                                    |
|    | 60-80                   | 87, 88, 89                            |
|    | 93 <sup>c</sup> ; 52-80 | 67 <sup>c</sup> , 72, 76, 87, 105     |
|    | 14-41                   | 90                                    |
|    | 36                      | 91                                    |
|   | —                       | 92                                    |
|  | 86                      | 93 <sup>b</sup>                       |
|  | 42-81                   | 93, 94, 95                            |
|  | 88                      | 7                                     |
|  | —                       | 96                                    |
|  | 65                      | 97                                    |
|  | 60                      | 94                                    |
|  | 77                      | 62, 63, 64                            |
|  | 62                      | 98                                    |
|  | 68-91                   | 72, 76, 99                            |
|  | 35                      | 18, 100                               |
|  | 22-41                   | 61, 101                               |
|  | 45                      | 99, 102                               |
|  | 75                      | 61, 91, 103, 104                      |
|  | 90                      | 61, 72, 76, 105                       |
|  | 52                      | 106                                   |

Table 3. Continued

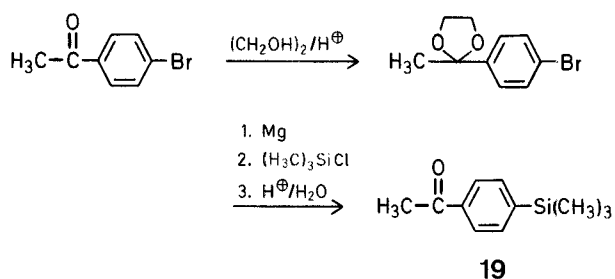
| Ar-X  | Yield [%] | Reference |
|---|-----------|-----------|
|  | 80        | 107       |
|  | —         | 108, 109  |
|  | 50        | 110, 111  |

<sup>a</sup> Polymers of product are also formed.

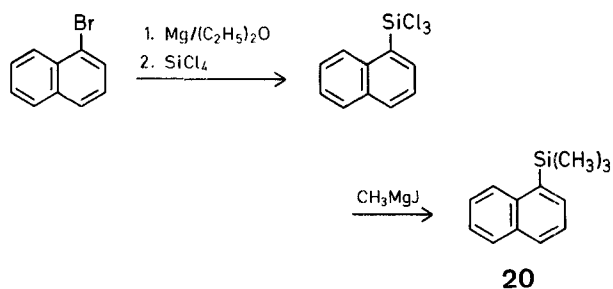
<sup>b</sup> Several trimethylsilylpolypheyl ethers are also formed.

<sup>c</sup> Bis[trimethylsilyl] product formed.

Diethyl ether is usually used as the solvent, although tetrahydrofuran is finding increasing use. Since the formation of Grignard function in sterically hindered positions (*o*-silylation) occurs only with difficulty, the ether can be replaced by some higher boiling solvent after the reaction has been started, to afford better yields<sup>61</sup>. Functional groups that react with Grignard reagents have to be protected, e.g. phenols by *O*-silylation<sup>62,63,64</sup> or carbonyl groups by acetalization. An example for the preparation of 4-acetylphenyltrimethylsilane (**19**) is illustrative<sup>65,66</sup>.



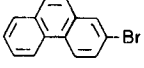
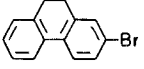
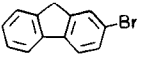
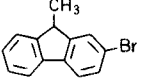
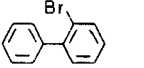
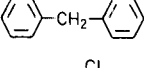
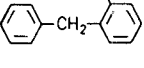
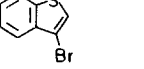
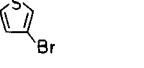
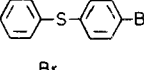

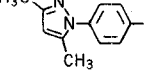
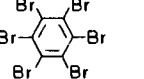
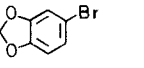
Haloaryltrimethylsilanes are obtained by selective silylation of polyhaloaromatic compounds, in the course of which the different reactivities of C—X bonds ( $J > \text{Br} > \text{Cl} > \text{F}$ ) towards magnesium are utilized. By using an excess of magnesium and chlorotrimethylsilane it is also possible to achieve bis-silylation<sup>67,68</sup>. The introduction of the trimethylsilyl groups via the trichlorosilyl compounds<sup>61,69,70,71</sup> is less often used but is illustrated by the preparation of 1-naphthyltrimethylsilane (**20**)<sup>60</sup>.



In some cases *inert* aryl halides which do not react well under conventional Grignard conditions can be converted to aryltrimethylsilanes in better yields by

using the *entrainment method*<sup>112</sup> (during the reaction some alkyl bromide is continuously added as an entrainer to keep the magnesium surface active (Table 4).

Table 4. Silylation of Aryl and Heteroaryl Halides via the Entrainment Method

































| Aryl Halide   | Entrainer                               | Yield [%]       | Reference |
|---|---|-----------------|-----------|
|    | Br—CH <sub>2</sub> —CH <sub>2</sub> —Br | 51              | 113       |
|    | Br—CH <sub>2</sub> —CH <sub>2</sub> —Br | 10              | 113       |
|    | Br—CH <sub>2</sub> —CH <sub>2</sub> —Br | 25              | 114, 115  |
|    | Br—CH <sub>2</sub> —CH <sub>2</sub> —Br | 31              | 115       |
|    | Br—CH <sub>2</sub> —CH <sub>2</sub> —Br | —               | 116       |
|   | Br—CH <sub>2</sub> —CH <sub>2</sub> —Br | 41              | 113, 114  |
|  | Br—CH <sub>2</sub> —CH <sub>2</sub> —Br | 21              | 97        |
|  | Br—CH <sub>2</sub> —CH <sub>2</sub> —Br | —               | 114       |
|  | C <sub>2</sub> H <sub>5</sub> —Br       | 50              | 117       |
|  | Br—CH <sub>2</sub> —CH <sub>2</sub> —Br | 60              | 114       |
|  | C <sub>2</sub> H <sub>5</sub> —Br       | —               | 118       |
|  | Br—CH <sub>2</sub> —CH <sub>2</sub> —Br | 80              | 119       |
|  | C <sub>2</sub> H <sub>5</sub> —Br       | 87 <sup>a</sup> | 120       |
|  | Br—CH <sub>2</sub> —CH <sub>2</sub> —Br | —               | 121       |

<sup>a</sup> Only the mono-silylated product is formed.

The separate preparation of the organometallic intermediates is often accompanied by disadvantages (e.g. isomerization, decomposition, more difficult *o*-silylation, etc.). These obstacles are reduced by bringing together the aryl halides with magnesium and chlorotrimethylsilane in a one pot reaction. The advantages of such an *in situ* procedure<sup>122</sup> have become obvious in the preparations of polysilylated benzenes<sup>123,124</sup> and naphthalene<sup>38</sup>, 2-halo-<sup>125,126,127</sup>, and some other phenyltrimethylsilanes<sup>128</sup> as well as in the reactions of 2-chloropyridine<sup>128,129,130</sup> and

-quinoline<sup>130</sup>. Particularly advantageous – even with sterically hindered compounds – is the *in situ* Grignard synthesis of aryltrimethylsilanes in hexamethylphosphoric triamide as solvent, as demonstrated by a recent publication which gives a comprehensive survey of the applications and limitations of this procedure (Table 5)<sup>131</sup>.

**Table 5.** *In Situ* Grignard Synthesis of Aryl- and Heteroaryltrimethylsilanes from Halides using Magnesium/Chlorotrimethylsilane/Hexamethylphosphoric Triamide<sup>131</sup>

| Aryl Halide   | Yield [%] | Aryl Halide   | Yield [%] |
|---|-----------|---|-----------|
|    | 87        |    | 61        |
|    | 88        |    | 67        |
|    | 80        |    | 76        |
|    | 85        |    | 33        |
|    | 81        |    | 71        |
|   | 83        |   | 73        |
|  | 85        |  | 75        |
|  | 62        |  | 74        |
|  | 49        |  | 41        |
|  | 58        |  | 75        |
|  | 74        |  | 72        |
|  | 80        |  | 76        |
|  | 67        |  | 62        |
|  | 31        |  | 78        |
|  | 77        |  | 32        |
|   |           |  | 49        |
|   |           |  | 78        |

#### 2-*t*-Butylphenyltrimethylsilane<sup>131</sup>:

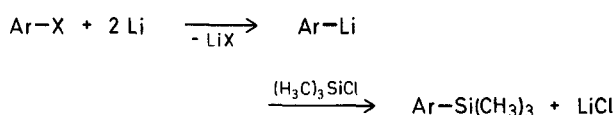
Magnesium (1.46 g, 0.06 mol), dry hexamethylphosphoric triamide (40 ml), and chlorotrimethylsilane (8.62 g, 0.08 mol) are placed in a two neck, round bottom flask equipped with a dropping funnel, condenser, and drying tube (phosphorus pentoxide). To this, a few ml of a solution of 2-*t*-butylbromobenzene (9.5 g, 0.044 mol) in dry hexamethylphosphoric triamide (15 ml) are added, the mixture is warmed until the contents begin to foam, and then the reaction is initiated by adding a few drops of 1,2-dibromoethane. The rest of

the aryl bromide solution is added with stirring within 5 h at 80°. stirring is then continued for 45 h at this temperature. After cooling, the reaction mixture is hydrolyzed by pouring into a 0.5% sodium hydrogen carbonate solution (250 ml), in the course of which the neutrality of the solution is tested. After the neutral mixture has been filtered by suction, the silane is extracted with ether, washed with water, dried with sodium sulfate, and fractionated; yield: 5.3 g (58%); b.p. 120°/130 torr;  $n_D^{20}$ : 1.5143.

#### 2.3.2. Preparations via Organolithium Compounds

Organolithium compounds are differentiated from the Grignard compounds by their greater reactivity and lesser steric sensitivity. The various procedures differ only in the preparation of the required lithium intermediate.

The reaction of aryl halides with metallic lithium, a method which is convenient in most cases only for less sensitive compounds (Table 6) has the closest similarity to the Grignard synthesis. Normally chlorotrimethylsilane is used as the silylating agent but in some cases the bromo and ethoxy derivatives have also been employed<sup>74, 132, 133</sup>.



**Table 6.** Aryltrimethylsilanes from Aryl Halides using Metallic Lithium/Chlorotrimethylsilane











| Aryl Halide   | Yield [%] | Reference                               |
|---|-----------|---|
|  | 67        | 108, 134, 135                           |
|  | 70        | 136                                     |
|  | 67        | 108, 134                                |
|  | 31-84     | 91, 108 <sup>a</sup> , 134 <sup>a</sup> |
|  | 53-72     | 75, 91, 108, 134, 137                   |
|  | 55-66     | 134 <sup>a</sup> , 138                  |
|  | 41-69     | 134 <sup>a</sup> , 138                  |
|  | 55-77     | 134 <sup>a</sup> , 138                  |
|  | 72-75     | 134 <sup>a</sup> , 138                  |
|  | 65-74     | 134 <sup>a</sup> , 138                  |

Table 6. Continued

| Aryl Halide | Yield [%]       | Reference              |
|-------------|-----------------|------------------------|
|             | 36-65           | 134 <sup>a</sup> , 138 |
|             | 75              | 139                    |
|             | 72 <sup>b</sup> | 139                    |
|             | 83              | 140                    |
|             | 71              | 141                    |
|             | 36              | 91                     |
|             | 40-55           | 91, 141                |
|             | 30              | 142                    |
|             | 45              | 143                    |
|             | 46-84           | 91, 143-146            |
|             | 29-79           | 91, 137, 144, 145      |
|             | 53              | 147                    |

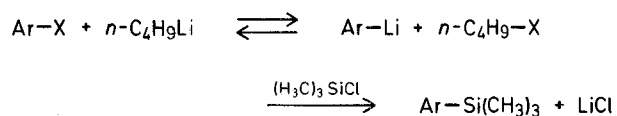
<sup>a</sup> Halide used for the preparation of the aryllithium not specified.

<sup>b</sup> Bis[trimethylsilyl] product obtained.

### 3-Dimethylaminophenyltrimethylsilane<sup>144</sup>:

To finely cut lithium (5.6 g, 0.81 mol) suspended in ether (100 ml), a solution of 3-bromodimethylaniline (70 g, 0.35 mol) is added with stirring over 2 h. The mixture is heated under reflux for 30 min, then a solution of chlorotrimethylsilane (37 g, 0.34 mol) in ether (75 ml) is added over 1 h. Stirring and heating under reflux are continued for 2 h. The reaction mixture is hydrolyzed, the ether layer separated, and dried with drierite. The mixture is filtered and the ether evaporated under reduced pressure. Distillation affords a colourless product; yield: 56 g (84%); b.p. 109–110°/8 torr;  $n_D^{20}$ : 1.5265.

Halide/metal exchange reactions present a further possibility for the preparation of aryllithium compounds.



The discrimination of reactivity of the C—X bond ( $J > \text{Br} > \text{Cl} > \text{F}$ ) toward *n*-butyllithium enables a selective exchange with polyhalogenated aromatic compounds (Table 7).

Table 7. Aryltrimethylsilanes via Halogen/Metal Exchange with *n*-Butyllithium and Subsequent Reaction with Chlorotrimethylsilane

| Aryl Halide | Yield [%]       | Reference |
|-------------|-----------------|-----------|
|             | 30              | 113       |
|             | 27              | 148       |
|             | 83 <sup>a</sup> | 149       |
|             | 46              | 77        |
|             | 46              | 77        |
|             | 58              | 77        |
|             | 58              | 77        |
|             | 35              | 150       |
|             | 20              | 150       |
|             | 53              | 150       |
|             | 48              | 150       |
|             | 70              | 151       |
|             | 50              | 152       |
|             | 72              | 152       |
|             | 67              | 152       |
|             | 70              | 152       |
|             | 36              | 94, 114   |
|             | 48              | 94        |
|             | 51              | 94        |



Table 7. Continued

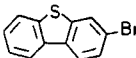
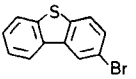
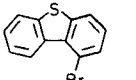
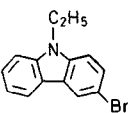
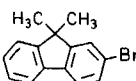
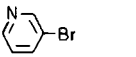
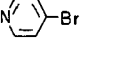
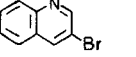
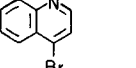
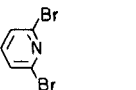
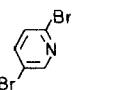
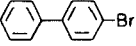
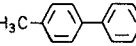
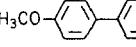
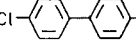
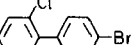
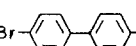
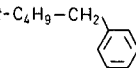
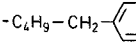
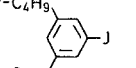
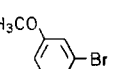
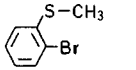
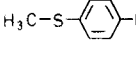
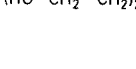
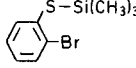
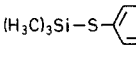
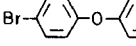
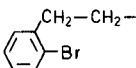
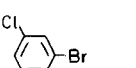
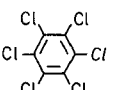
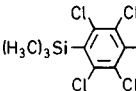
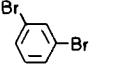
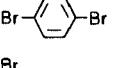
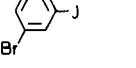
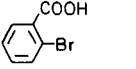
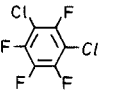
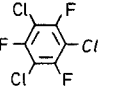
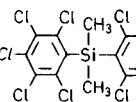
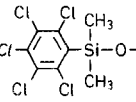
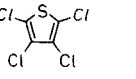
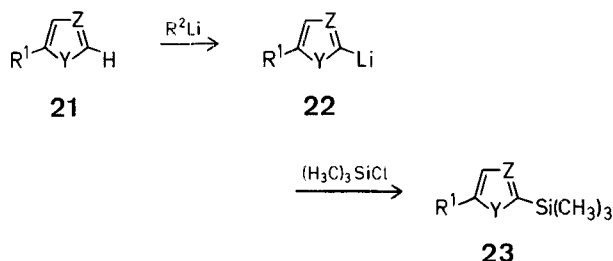
| Aryl Halide   | Yield [%]           | Reference     |
|---|---------------------|---------------|
|    | 50-71               | 94, 153       |
|    | 64-80               | 94, 153       |
|    | 45                  | 94            |
|    | 77                  | 94            |
|    | 68                  | 115           |
|    | 24-39               | 129, 130, 154 |
|    | 37-39               | 129, 130      |
|   | 49                  | 130           |
|  | 36                  | 130           |
|  | 91, 90 <sup>a</sup> | 155, 342      |
|  | 69 <sup>a</sup>     | 342           |
|  | 37-65               | 77            |
|  | 64-78               | 156, 157, 158 |
|  | 43                  | 157           |
|  | 72-80               | 156, 157      |
|  | 65                  | 156           |
|  | 43                  | 157           |
|  | 70                  | 159           |
|  | 80                  | 159           |
|  | —                   | 108           |
|  | 27                  | 108           |

Table 7. Continued

| Aryl Halide   | Yield [%]           | Reference                  |
|---|---------------------|----------------------------|
|    | 64                  | 97                         |
|    | 65                  | 97                         |
|    | 51                  | 160                        |
|    | —                   | 97                         |
|    | 20-80               | 97, 161                    |
|    | 77 <sup>a</sup>     | 162                        |
|    | 80                  | 163                        |
|    | 62                  | 91                         |
|   | 48, 44 <sup>a</sup> | 164, 165, 166 <sup>a</sup> |
|  | —                   | 167                        |
|  | 17                  | 85, 168                    |
|  | 47-79               | 145, 169, 170              |
|  | 33                  | 108                        |
|  | 57                  | 168                        |
|  | —                   | 171 <sup>b</sup>           |
|  | 87                  | 171 <sup>b</sup>           |
|  | 17 <sup>a</sup>     | 167                        |
|  | 13 <sup>a</sup>     | 167                        |
|  | 80 <sup>a</sup>     | 172                        |

<sup>a</sup> Bis[trimethylsilyl] product obtained.<sup>b</sup> Use of excess *n*-butyllithium and chlorotrimethylsilane results in formation of polytrimethylsilylated products.

The more strongly acidic C-H bonds of heteroaromatic compounds such as, for example **21**, can be metallated directly by treatment with organolithium compounds and subsequently silylated to yield silanes **23** without the need for the intermediate halogenated compounds (Table 8).



**Table 8.** Heteroaryltrimethylsilanes **23** via Hydrogen/Metal Exchange in **21** with *n*-Butyllithium and Subsequent Silylation

| Substrate <b>21</b><br>R <sup>1</sup>                           | Y  | Z                   | Yield [%]<br>of <b>23</b> | Reference |
|---|----|---------------------|---------------------------|-----------|
| H   | O  | CH                  | —                         | 94        |
| H   | O  | C—Br                | — <sup>a</sup>            | 173       |
| H   | S  | CH                  | —                         | 94, 117   |
| H <sub>3</sub> C  | S  | CH                  | 72                        | 175       |
| (H <sub>3</sub> C) <sub>2</sub> N—SO <sub>2</sub>               | S  | CH                  | 41                        | 176       |
| (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> N—SO <sub>2</sub> | S  | CH                  | 79                        | 176       |
| Br  | S  | CH                  | — <sup>a</sup>            | 173       |
| H   | S  | C—COOH              | — <sup>a</sup>            | 173       |
| (C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> CH               | S  | CH                  | 93                        | 177       |
|   | S  | CH                  | 96                        | 177, 178  |
| (C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)             | S  | CH                  | 31                        | 179       |
| H   | NH | CH                  | 23–40                     | 180, 181  |
| H   | N  | CH <sub>3</sub> , N | 33–56                     | 182, 183  |

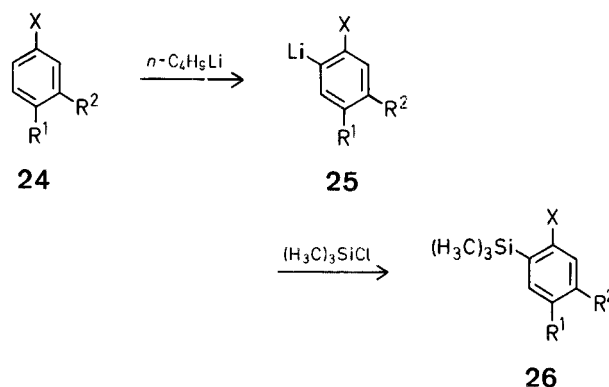
<sup>a</sup> Lithium diisopropylamide is used as metallating agent.

In this manner, 2,5-bis[trimethylsilyl]thiophene (65%) is obtained from thiophene<sup>175</sup> by reaction with two mol of butyllithium/chlorotrimethylsilane and *N*-methyl-1,4-bis[trimethylsilyl]imidazole (32%) may be prepared from *N*-methylimidazole<sup>182</sup>. This method of silylation is also applicable to benzo-annulated systems, e.g. benzothiophene<sup>94, 114</sup>, -thiazole<sup>184, 185</sup>, and -imidazole<sup>182, 183</sup>.

#### Trimethyl-(1-methyl-2-imidazolyl)-silane<sup>182</sup>:

1-Methylimidazole (9.58 g, 120 mmol) is slowly added (dropwise) to a hexane solution of *n*-butyllithium (120 mmol) in ether (150 ml). After heating under reflux for 1h, chlorotrimethylsilane (13.03 g, 120 mmol) is added. After 2 h of stirring, the reaction mixture is filtered, the solvent evaporated, and the silane isolated by vacuum distillation; yield: 10.3 g (56%); b.p. 92°/10 torr.

Besides the heterocyclic compounds **21**, benzene derivatives **24**, in which *ortho*-metallation<sup>186</sup> is favoured by appropriate substituents, can also be metallated directly and subsequently silylated to afford aryltrimethylsilanes **26** (Table 9).



**Table 9.** Aryltrimethylsilanes **26** via *ortho*-Metallation of Benzene Derivatives **24**

| Substrate <b>24</b> |                  |   | Yield [%]<br>of <b>26</b> | Reference   |
|---------------------|------------------|---|---------------------------|-------------|
| R <sup>1</sup>      | R <sup>2</sup>   | X   |                           |             |
| H                   | H                | OC <sub>6</sub> H <sub>5</sub>                          | 62–71                     | 93, 94, 114 |
| H                   | H                | SC <sub>6</sub> H <sub>5</sub>                          | 23                        | 94, 114     |
| F                   | H                | OCH <sub>3</sub>  | 13                        | 187         |
| Cl                  | H                | OCH <sub>3</sub>  | 60                        | 187         |
| Br                  | H                | OCH <sub>3</sub>  | 44                        | 187         |
| J                   | H                | OCH <sub>3</sub>  | 58                        | 187         |
| H                   | H                | CH <sub>2</sub> —N(CH <sub>3</sub> ) <sub>2</sub>       | 60                        | 188         |
| H                   | H                | CO—NH—C <sub>6</sub> H <sub>5</sub>                     | 60                        | 189         |
| H                   | H                | C[O—Si(CH <sub>3</sub> ) <sub>3</sub> ]—CH <sub>2</sub> | 90 <sup>a</sup>           | 190         |
| H <sub>3</sub> C    | H                | C[O—Si(CH <sub>3</sub> ) <sub>3</sub> ]—CH <sub>2</sub> | 71 <sup>a, b</sup>        | 190         |
| H                   | H <sub>3</sub> C | C[O—Si(CH <sub>3</sub> ) <sub>3</sub> ]—CH <sub>2</sub> | 90 <sup>a</sup>           | 190         |

<sup>a</sup> *n*-Butyllithium/tetramethylethylenediamine used as metallating agent.

<sup>b</sup> Two products arising from dimetallation also formed (yield: 10% each).

The intramolecular complexation of the lithium compound **25** is decisive. Since the complexation is also possible with the other *ortho*-position, bis-silylated compounds, such as 2,2'-bis[trimethylsilyl]diphenyl ether (60%)<sup>162</sup> or 2,6-bis[trimethylsilyl]-*N,N*-dimethylbenzylamine (85%)<sup>188</sup>, can be produced selectively. In the cases of phloroglucine trimethyl ether<sup>191</sup>, methoxy-*n*-phthalenes<sup>150</sup>, and dibenzofuran<sup>94</sup> reaction can be brought about specifically. Aromatic compounds without such C-H bonds react to form mixtures of isomers<sup>192, 116</sup>. Thus polymetallation/silylation reactions of aromatic compounds such as biphenyl, anthracene, fluorene etc. with butyllithium/tetramethylethylenediamine/chlorotrimethylsilane are of no preparative importance<sup>193</sup>.

There is the possibility of a competition between metal/halogen exchange (formation of **28**) and metal/hydrogen exchange (formation of **29**) in the case of the polyhaloaromatic compounds **27** (Table 10).

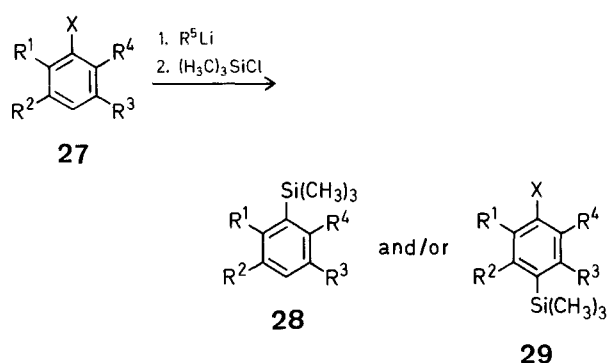
Once again polysilylated products are formed when an excess of organolithium compound (R<sup>5</sup>Li)/chlorotrimethylsilane is employed<sup>194, 197, 198, 199</sup>.

**Table 10.** Competition of Metal/Halogen and Metal/Hydrogen Exchange in Polyhaloaromatic Compounds 27

| R <sup>1</sup> | R <sup>2</sup> | R <sup>3</sup> | R <sup>4</sup> | X  | R <sup>5</sup>                          | Yield [%] of |                 | Reference     |
|----------------|----------------|----------------|----------------|----|---|--------------|-----------------|---------------|
|                |                |                |                |    |   | 28           | 29              |               |
| Cl             | H              | Cl             | Cl             | Cl | <i>t</i> -C <sub>4</sub> H <sub>9</sub> | 100          | —               | 165, 194, 195 |
| Cl             | H              | Cl             | Cl             | Cl | <i>n</i> -C <sub>4</sub> H <sub>9</sub> | 71           | 29              | 165, 194, 195 |
| Cl             | H              | Cl             | Cl             | Cl | C <sub>6</sub> H <sub>5</sub>           | 10           | 90              | 165, 194, 195 |
| Cl             | H              | Cl             | Cl             | Cl | CH <sub>3</sub>                         | 7            | 93              | 165, 194, 195 |
| Cl             | H              | H              | Cl             | Cl | <i>t</i> -C <sub>4</sub> H <sub>9</sub> | 100          | —               | 194, 195      |
| Cl             | H              | H              | Cl             | Cl | <i>n</i> -C <sub>4</sub> H <sub>9</sub> | 65           | 35              | 194, 195      |
| Cl             | Cl             | Cl             | Cl             | Cl | <i>t</i> -C <sub>4</sub> H <sub>9</sub> | 38           | 45 <sup>a</sup> | 194           |
| Cl             | Cl             | Cl             | Cl             | Cl | <i>n</i> -C <sub>4</sub> H <sub>9</sub> | —            | 95              | 194           |
| F              | F              | Br             | F              | F  | <i>n</i> -C <sub>4</sub> H <sub>9</sub> | —            | 87              | 196           |
| H              | F              | F              | H              | F  | <i>n</i> -C <sub>4</sub> H <sub>9</sub> | —            | — <sup>b</sup>  | 197           |

<sup>a</sup> 3,6-Bis[trimethylsilyl]-1,2,4,5-tetrachlorobenzene [29: X = Si(CH<sub>3</sub>)<sub>3</sub>, R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = Cl] also formed in 17% yield.

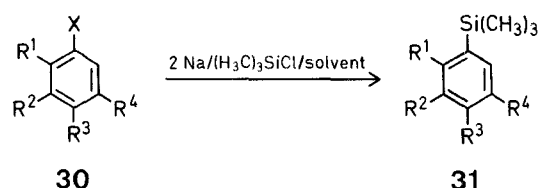
<sup>b</sup> Mono-, bis-, and tris[trimethylsilyl] compounds are formed.



tives. The silylation is therefore normally carried out in a manner analogous to the Wurtz-Fittig reaction and not by the use of isolated sodium compounds. Ether, benzene, toluene, or xylene can be used as solvents. The rigorous reaction conditions allow only for the presence of inert substituents (e.g. alkyl-, aryl-, alkoxy-, aryloxy-, R<sub>3</sub>Si-groups etc.). Phenols and anilines have to be protected by *O*- or *N*-silylation, respectively before the Wurtz coupling reaction can be performed (Table 11).

### 2.3.3. Preparations via Organosodium Compounds

Organosodium compounds are even more reactive and sensitive than the comparable lithium deriva-

**Table 11.** Aryltrimethylsilanes 31 via Wurtz Coupling of Aryl Halides 30 with Chlorotrimethylsilane/Sodium/Solvent

| R <sup>1</sup>  | R <sup>2</sup>                          | R <sup>3</sup>  | R <sup>4</sup>                          | X  | Solvent                                 | Yield [%] of 31 | Reference                  |
|-----------------|---|-----------------|---|----|---|-----------------|----------------------------|
| H               | H                                       | H               | H                                       | Cl | toluene <sup>a</sup> or ether           | 65–90           | 102, 200, 201              |
| H               |   | H               | H                                       | Br | toluene                                 | 27              | 94                         |
| CH <sub>3</sub> | H                                       | H               | H                                       | Cl | toluene                                 | 68              | 168, 102                   |
| H               | CH <sub>3</sub>                         | H               | H                                       | Cl | toluene, ether <sup>a</sup> , or xylene | 55–85           | 61, 201 <sup>a</sup> , 202 |
| H               | H                                       | CH <sub>3</sub> | H                                       | Cl | toluene                                 | 87              | 102                        |
| CH <sub>3</sub> | CH <sub>3</sub>                         | H               | H                                       | Cl | benzene or toluene                      | 74              | 203, 204                   |
| CH <sub>3</sub> | H                                       | CH <sub>3</sub> | H                                       | Cl | toluene                                 | —               | 203                        |
| CH <sub>3</sub> | H                                       | H               | CH <sub>3</sub>                         | Cl | toluene                                 | —               | 203                        |
| CH <sub>3</sub> | H                                       | H               | CH <sub>3</sub>                         | Br | benzene                                 | 74              | 204                        |
| H               | CH <sub>3</sub>                         | CH <sub>3</sub> | H                                       | Cl | benzene or toluene                      | 75              | 203, 204                   |
| H               | CH <sub>3</sub>                         | H               | CH <sub>3</sub>                         | Br | benzene or toluene                      | 81              | 203, 204                   |
| H               | C <sub>2</sub> H <sub>5</sub>           | H               | H                                       | Cl | ether <sup>a</sup>                      | 50              | 201 <sup>a</sup>           |
| H               | C <sub>2</sub> H <sub>5</sub>           | H               | C <sub>2</sub> H <sub>5</sub>           | Br | ether                                   | 77              | 108                        |
| H               | <i>i</i> -C <sub>3</sub> H <sub>7</sub> | H               | H                                       | Br | ether                                   | 75              | 201                        |
| H               | <i>i</i> -C <sub>3</sub> H <sub>7</sub> | H               | <i>i</i> -C <sub>3</sub> H <sub>7</sub> | Br | —                                       | —               | 108                        |

Table 11. Continued

| R <sup>1</sup>                      | R <sup>2</sup>                                      | R <sup>3</sup>  | R <sup>4</sup>                     | X  | Solvent                       | Yield [%]<br>of 31 | Reference              |
|-------------------------------------|---|---|------------------------------------|----|-------------------------------|--------------------|------------------------|
| H                                   | <i>t</i> -C <sub>4</sub> H <sub>9</sub>             | H   | H                                  | Cl | ether <sup>a</sup> or toluene | 55–67              | 85, 201 <sup>a</sup>   |
| H                                   | H   | <i>t</i> -C <sub>4</sub> H <sub>9</sub>   | H                                  | Cl | ether                         | 26                 | 81                     |
|                                     | —(CH <sub>2</sub> ) <sub>2</sub> —                  | H   | H                                  | Cl | toluene <sup>a</sup>          | 58                 | 152                    |
|                                     | —(CH <sub>2</sub> ) <sub>3</sub> —                  | H   | H                                  | Cl | toluene <sup>a</sup>          | 73                 | 152                    |
|                                     | (CH <sub>2</sub> ) <sub>4</sub> —                   | H   | H                                  | Cl | toluene <sup>a</sup>          | 50                 | 152                    |
| C <sub>6</sub> H <sub>5</sub>       | H   | H   | H                                  | Cl | toluene                       | 77                 | 61, 205                |
| H                                   | C <sub>6</sub> H <sub>5</sub>                       | H   | H                                  | Cl | toluene                       | 77                 | 205                    |
| (H <sub>3</sub> C) <sub>3</sub> Si  | H   | H   | H                                  | Cl | toluene                       | 58–77              | 61, 142, 206           |
| H                                   | (H <sub>3</sub> C) <sub>3</sub> Si                  | H   | H                                  | Cl | toluene                       | 52–85              | 61, 85, 206            |
| H                                   | H   | (H <sub>3</sub> C) <sub>3</sub> Si  | H                                  | Cl | toluene                       | 26–68              | 61, 81, 206, 124       |
| H                                   | H   | 4-(H <sub>3</sub> C) <sub>3</sub> Si—C <sub>6</sub> H <sub>4</sub>                  | H                                  | Cl | toluene                       | 80                 | 157                    |
| H                                   | H   | 4-Br—C <sub>6</sub> H <sub>4</sub>  | H                                  | Br | toluene                       | <sup>b</sup>       | 206                    |
| H                                   | H <sub>3</sub> CO                                   | H   | H                                  | Cl | ether <sup>a</sup> or toluene | 50–65              | 108 <sup>a</sup> , 202 |
| H                                   | H <sub>3</sub> CO                                   | H <sub>3</sub> CO   | H                                  | Br | toluene                       | —                  | 121                    |
| H                                   | O—(CH <sub>2</sub> ) <sub>2</sub> —O                | H   | H                                  | Br | toluene                       | —                  | 121                    |
| H <sub>3</sub> CO                   | H   | H   | (H <sub>3</sub> C) <sub>3</sub> Si | Cl | toluene                       | 84                 | 207                    |
| H                                   | H   | C <sub>n</sub> H <sub>2n+1</sub> O <sup>c</sup>                                     | H                                  | Cl | toluene                       | 74–82              | 208                    |
| H                                   | H   | C <sub>6</sub> H <sub>5</sub> O   | H                                  | Cl | toluene                       | 59                 | 94, 114                |
| H                                   | H   | (H <sub>3</sub> C) <sub>3</sub> Si—O—CH—CH <sub>2</sub> —O—<br> <br>CH <sub>3</sub> | H                                  | Cl | toluene                       | —                  | 209                    |
| (H <sub>3</sub> C) <sub>3</sub> SiO | H   | H   | H                                  | Cl | toluene                       | 94                 | 210                    |
| H                                   | (H <sub>3</sub> C) <sub>3</sub> SiO                 | H   | H                                  | Cl | toluene                       | 70–85              | 85, 144                |
| H                                   | H   | (H <sub>3</sub> C) <sub>3</sub> SiO   | H                                  | Cl | toluene                       | 84                 | 210                    |
| (H <sub>3</sub> C) <sub>3</sub> SiO | H   | (H <sub>3</sub> C) <sub>3</sub> SiO   | H                                  | Cl | toluene                       | 98                 | 210                    |
| H                                   | C <sub>6</sub> H <sub>5</sub>                       | (H <sub>3</sub> C) <sub>3</sub> SiO   | H                                  | Cl | toluene                       | 76                 | 210, 211               |
| (H <sub>3</sub> C) <sub>3</sub> SiO | C <sub>6</sub> H <sub>5</sub>                       | H   | H                                  | Cl | toluene                       | —                  | 210, 211               |
| H                                   | [(H <sub>3</sub> C) <sub>3</sub> Si] <sub>2</sub> N | H   | H                                  | Cl | toluene                       | 73                 | 147                    |

<sup>a</sup> Sodium suspension.<sup>b</sup> Bis[trimethylsilyl] product formed.<sup>c</sup> n = 4, 8, 12, 14, 16, 18.

1- and 2-Chloronaphthalene<sup>212</sup> as well as various chloro- and bromophenanthrenes<sup>113</sup> react in a similar way. The partial reaction of polyhaloaromatic compounds is not possible: either all halide atoms react<sup>213</sup> or the molecule does not undergo a Wurtz coupling<sup>61</sup>. Numerous 2,4,6-substituted silylated phenols have been prepared according to this method<sup>214, 215</sup>.

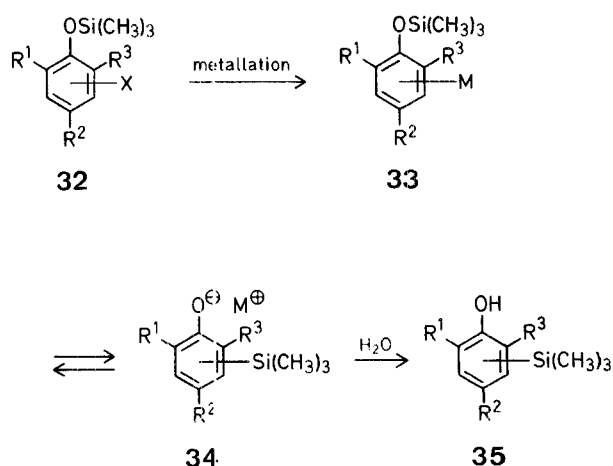
#### *o*-Tolyltrimethylsilane<sup>162</sup>:

*o*-Chlorotoluene (502.5 g, 3.95 mol) is mixed with chlorotrimethylsilane (see below) and added slowly to molten sodium (195 g, 8.5 mol) in boiling toluene [400 ml, containing sufficient chlorotrimethylsilane to lower the reflux temperature to 102°]. A total of 475 g (4.4 mol) of chlorotrimethylsilane is employed]. The reaction is vigorous; when the reaction is complete, the reaction mixture is diluted with ethanol (to destroy excess sodium), washed with water and distilled; yield: 600 g (87%); b.p. 94.4°/23 torr; n<sub>D</sub><sup>25</sup>: 1.5016; d<sub>4</sub><sup>25</sup>: 0.8840.

Up to now examples of the formation of carbon-silicon bonds via organozinc and -aluminum compounds have only been reported with aliphatic compounds. For the preparation of aryltrimethylsilanes the system of zinc dust/chlorotrimethylsilane/hexamethylphosphoric triamide offers no advantages compared to the procedures described in Sections 2.3.1., 2.3.2., and 2.3.3.<sup>131</sup>

#### 2.3.4. Preparations via Rearrangements

The silylation of organometallic compounds can also be achieved via rearrangements, i.e. without external silylating agents such as chlorotrimethylsilane. Thus, the halophenoxytrimethylsilanes **32**, after metallation with butyllithium or magnesium to give **33**, rearrange to the silylated phenolates **34**, the hydrolysis of which affords the phenols **35**<sup>216–220</sup> (Table 12).



**Table 12.** Trimethylsilyl-Substituted Phenols **35** via Rearrangement of Metallated Phenoxytrimethylsilanes **33**

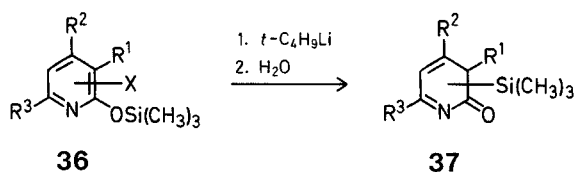
| Substrate <b>32</b><br>R <sup>1</sup> | R <sup>2</sup>                          | R <sup>3</sup>                          | X    | Metallating agent                          | Yield [%] of <b>35</b> | Reference    |
|---------------------------------------|---|---|------|--|------------------------|--------------|
| —                                     | H                                       | H                                       | 2-Br | <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li | 20–86                  | 97, 161, 216 |
| —                                     | H                                       | H                                       | 2-Br | <i>t</i> -C <sub>4</sub> H <sub>9</sub> Li | 100 <sup>a</sup>       | 217          |
| H                                     | H                                       | H                                       | 3-Br | Mg   | 80                     | 218          |
| H                                     | —                                       | H                                       | 4-Br | <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li | 80                     | 97, 216      |
| H                                     | —                                       | H                                       | 4-Br | <i>t</i> -C <sub>4</sub> H <sub>9</sub> Li | 87 <sup>a</sup>        | 217          |
| H                                     | —                                       | H                                       | 4-Br | Mg   | 17 <sup>b</sup>        | 218          |
| —                                     | H <sub>3</sub> C                        | H                                       | 2-Br | <i>t</i> -C <sub>4</sub> H <sub>9</sub> Li | 93                     | 217          |
| H <sub>3</sub> C                      | —                                       | H                                       | 4-Br | <i>t</i> -C <sub>4</sub> H <sub>9</sub> Li | 80                     | 217          |
| —                                     | <i>t</i> -C <sub>4</sub> H <sub>9</sub> | H                                       | 2-Br | <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li | 96                     | 219          |
| —                                     | <i>t</i> -C <sub>4</sub> H <sub>9</sub> | H                                       | 2-Br | Mg   | 80                     | 218          |
| —                                     | <i>t</i> -C <sub>4</sub> H <sub>9</sub> | <i>t</i> -C <sub>4</sub> H <sub>9</sub> | 2-Br | <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li | 95                     | 219, 220     |
| —                                     | <i>t</i> -C <sub>4</sub> H <sub>9</sub> | <i>t</i> -C <sub>4</sub> H <sub>9</sub> | 2-Br | Mg   | 85                     | 218          |
| —                                     | Br                                      | <i>t</i> -C <sub>4</sub> H <sub>9</sub> | 2-Br | <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li | 85                     | 219          |
| —                                     | Br                                      | Br                                      | 2-Br | <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li | 92                     | 219          |
| —                                     | Br                                      | Br                                      | 2-Br | Mg   | 25 <sup>b</sup>        | 218          |
| —                                     | <i>t</i> -C <sub>4</sub> H <sub>9</sub> | (H <sub>3</sub> C) <sub>3</sub> Si      | 2-Br | Mg   | 70                     | 218          |
| —                                     | H                                       | (H <sub>3</sub> C) <sub>3</sub> Si      | 2-Br | Mg   | 84                     | 218          |
| —                                     | H                                       | Br                                      | 2-Br | Mg   | 6                      | 218          |
| —                                     | <i>t</i> -C <sub>4</sub> H <sub>9</sub> | Br                                      | 2-Br | Mg   | 83                     | 218          |
| —                                     | H <sub>3</sub> C                        | <i>t</i> -C <sub>4</sub> H <sub>9</sub> | 2-Br | <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li | 90                     | 220          |
| —                                     | Cl                                      | Cl                                      | 2-Br | <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li | 77                     | 220          |
| —                                     | <i>t</i> -C <sub>4</sub> H <sub>9</sub> | Br                                      | 2-J  | <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li | 88                     | 220          |

<sup>a</sup> Yield determined by G.L.C./M.S.

<sup>b</sup> Obtained as mixture with other products.

Repeated application of this process to polyhalogenated compounds **32** as well as the working up of **34** with agents other than water provides further preparative possibilities<sup>218</sup>.

These derivatives can undergo rearrangement to give trimethylsilyl-substituted thiophenols in the same way<sup>161,97</sup>, however, the rearrangement of *N*-silylated haloanilines fails<sup>147,216</sup>. The rearrangement method can also be used with some pyridines **36** to yield trimethylsilyl-2-pyridones **37** without difficulties<sup>217</sup> (Table 13).

**Table 13.** Trimethylsilyl-Substituted 2-Pyridones<sup>a</sup> **37** via Rearrangement of Pyridines **36** using *t*-Butyllithium<sup>217</sup>

| Substrate <b>36</b><br>R <sup>1</sup> | R <sup>2</sup>                | R <sup>3</sup>   | X    | Yield [%] of <b>37</b> |
|---------------------------------------|-------------------------------|------------------|------|------------------------|
| —                                     | H                             | H                | 3-Br | 62                     |
| H                                     | H                             | H                | 5-Br | 51                     |
| H <sub>3</sub> C                      | H                             | H                | 5-Br | 98                     |
| H                                     | H                             | H <sub>3</sub> C | 5-Br | 47                     |
| H                                     | C <sub>6</sub> H <sub>5</sub> | —                | 6-Br | 69                     |

<sup>a</sup> In the same way, *O*- and *N*-trimethylsilylated pyrimidines can be rearranged to the *C*-silylated compounds<sup>216,221</sup>.

Another *O*→*C* migration of the trimethylsilyl group was observed for 4-trimethylsilylcoumarin<sup>222</sup>. The apparent *N*→*C* migration upon silylation of the pyrrole anion<sup>180</sup> is presently explained as a double silylation with subsequent solvolysis of the sensitive nitrogen-silicon bond<sup>181</sup>. The acid-catalyzed (trifluoroacetic acid) isomerization of 1,2-bis[trimethylsilyl]benzene to the 1,3-isomer, which occurs on heating at 150° for 48 h in a sealed tube<sup>223,224</sup>, is explained by a normal  $\sigma$ -complex mechanism. Surprisingly the catalyst does not seem to be consumed by protodesilylation, as expected according to a recent paper<sup>57</sup>. Indeed the isomerization also proceeds using 5 mol-% trimethylsilyl trifluoroacetate under the same conditions<sup>57</sup>. Isomerizations of this type, also catalyzed by other agents, have been observed, but not thoroughly investigated<sup>149,225,226</sup>.

### 3. Synthesis of Aryl- and Heteroaryltrimethylsilanes via Cycloaddition Reactions

Silylated aromatic and heteroaromatic compounds can be synthesized from appropriately substituted unsaturated compounds. Little advantage has been taken of the possibility of preparing aryl- and heteroaryltrimethylsilanes in this way. Interesting developments should be expected, especially in the preparation of silylated heterocycles.

### 3.1. Aryltrimethylsilanes via [2 + 2 + 2]Cycloaddition Reactions

Cooligomerization of diynes **38** with acetylenes **39** in the presence of cobalt catalysts is a general synthesis for trimethylsilyl-substituted benzocyclobutenes, indanes, tetralins **40**, or naphthalenes **41** (Table 14).

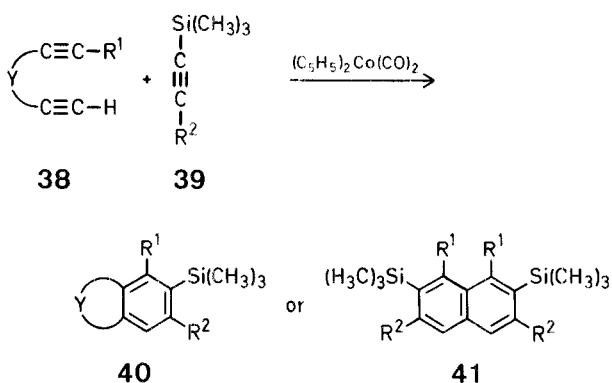


Table 14. Trimethylsilyl-Substituted Benzocycloalkanes **40** or Naphthalenes **41** via [2 + 2 + 2] Cycloaddition Reactions

| Diyne <b>38</b>                    | Acetylene <b>39</b>                                       | Product                                      | Yield | Reference |
|------------------------------------|---|--|-------|-----------|
| R <sup>1</sup>                     | Y   | type   | [%]   |           |
| H                                  | (CH <sub>2</sub> ) <sub>2</sub>                           | (H <sub>3</sub> C) <sub>3</sub> Si <b>40</b> | 60    | 226       |
| (H <sub>3</sub> C) <sub>3</sub> Si | (CH <sub>2</sub> ) <sub>2</sub>                           | H <b>40</b>                                  | 22    | 227       |
| H                                  | (CH <sub>2</sub> ) <sub>3</sub>                           | (H <sub>3</sub> C) <sub>3</sub> Si <b>40</b> | 50    | 225       |
| H                                  | (CH <sub>2</sub> ) <sub>4</sub>                           | (H <sub>3</sub> C) <sub>3</sub> Si <b>40</b> | 49    | 225       |
| H                                  | (CH <sub>2</sub> ) <sub>4</sub>                           | H <sub>3</sub> C <b>40</b>                   | 34    | 225       |
| H                                  | CH—CH <sub>2</sub>  | (H <sub>3</sub> C) <sub>3</sub> Si <b>41</b> | 30    | 228       |
| H                                  | OSi(CH <sub>3</sub> ) <sub>3</sub><br>—CH—CH <sub>2</sub> | (H <sub>3</sub> C) <sub>3</sub> Si <b>41</b> | 30    | 228       |
| H                                  | OCH <sub>3</sub><br>—CH—CH <sub>2</sub>                   | (H <sub>3</sub> C) <sub>3</sub> Si <b>41</b> | 30    | 228       |

2-Thp<sup>a</sup>

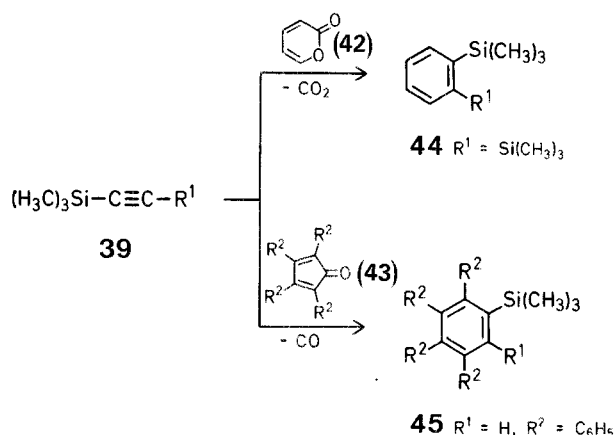
<sup>a</sup> Thp = 2-tetrahydropyranyl.

The cyclotrimerization of trimethylsilylacetylenes in the presence of cobalt catalysts<sup>229</sup> or the system titanium(IV) chloride/trimethylaluminum<sup>230</sup> is difficult to direct and normally affords isomer mixtures of polysilylated benzenes.

### 3.2. Aryl- and Heteroaryltrimethylsilanes via [4 + 2]Cycloaddition Reactions

Cycloaddition reactions of  $\alpha$ -pyrone (**42**) or tetraphenylcyclopentadienone (**43**) with trimethylsilylacetylenes **39** lead to aryltrimethylsilanes **44** (63%)<sup>231</sup> or **45** (90%)<sup>232</sup>, respectively.

Very strained systems such as trimethylsilyl-substituted benzocyclobutenes and -butadienes undergo



ring-expansion on treatment with alkenes and alkynes to afford tetralins<sup>226</sup> and naphthalenes<sup>174</sup> of types otherwise not readily obtainable. The addition of **39** [R<sup>1</sup> = H, Si(CH<sub>3</sub>)<sub>3</sub>] to 3,6-bis[methoxycarbonyl] 1,2,4,5-tetrazine gives C-silylated pyridazines (70–85%) with elimination of nitrogen<sup>233</sup>.

### 3.3. Heteroaryltrimethylsilanes via [2 + 3]Cycloaddition Reactions

The pyrazolyltrimethylsilanes **47–49** are readily obtained in good yields by the cycloaddition of trimethylsilylacetylenes **39** to diazomethane derivatives **46** (Table 15).

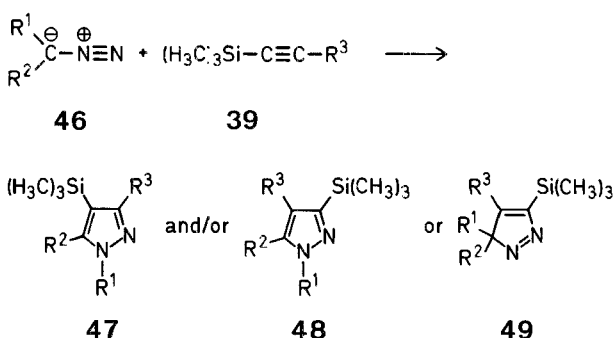


Table 15. Trimethylsilyl-Substituted Pyrazoles **47–49** via [2 + 3]Cycloaddition Reactions

| Diazomethane <b>46</b> | Alkyne <b>39</b>                  | Product                            | Yield          | Reference |          |
|------------------------|-----------------------------------|------------------------------------|----------------|-----------|----------|
| R <sup>1</sup>         | R <sup>2</sup>                    | R <sup>3</sup>                     | type           | [%]       |          |
| H                      | H                                 | H                                  | <b>48</b>      | 100       | 234, 235 |
| H                      | H                                 | C <sub>6</sub> H <sub>5</sub>      | <b>48</b>      | 20–25     | 234, 236 |
| H                      | H                                 | CH <sub>3</sub>                    | <b>48</b>      | 1         | 234      |
| H                      | H                                 | (H <sub>3</sub> C) <sub>3</sub> Si | <b>48</b>      | 60–95     | 234, 236 |
| H                      | H                                 | HOCH <sub>2</sub>                  | <b>48</b>      | 40        | 234      |
| H                      | C <sub>2</sub> H <sub>5</sub> OOC | (H <sub>3</sub> C) <sub>3</sub> Si | <b>48</b>      | 92        | 236      |
| H                      | C <sub>2</sub> H <sub>5</sub> OOC | H                                  | <b>48</b>      | 99        | 235      |
| H                      | H                                 | O—CH                               | <b>47 + 48</b> | 28 + 72   | 234      |
| H                      | H                                 | H <sub>3</sub> COOC                | <b>47 + 48</b> | 20 + 80   | 234      |
| H                      | H                                 | H <sub>3</sub> C—CO                | <b>47 + 48</b> | 30 + 70   | 235      |
| H <sub>3</sub> C       | H <sub>3</sub> C                  | H <sub>3</sub> COOC                | <b>49</b>      | 100       | 234      |

In the case of tautomeric compounds (R<sup>1</sup> = H) the orientation of the addition proceeds with high re-

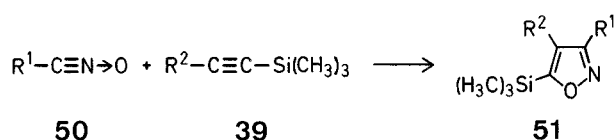
gioselectivity to afford predominantly the pyrazoles **48**. This is probably due more to steric than to electronic factors<sup>23,4</sup>.

Using this method, trimethylsilyl groups can also be introduced via a [2+3]cycloaddition reaction as shown by the reaction of bis[trimethylsilyl]diazomethane with acetylenedicarboxylic ester. One trimethylsilyl group migrates to the nitrogen atom, yielding the corresponding pyrazole (73%)<sup>23,7</sup>.

### 3-Pyrazolyltrimethylsilane (**48**; R<sup>1</sup>-R<sup>3</sup> = H)<sup>23,5</sup>:

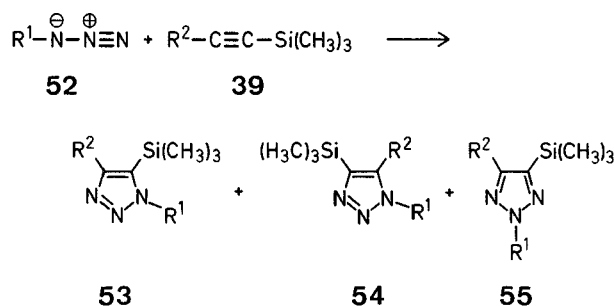
Trimethylsilylacetylene (4.91 g, 50 mmol) and diazomethane (70 mmol) in dry ether (100 ml) are kept in the dark for 3 days at room temperature. After the destruction of excess diazomethane by short boiling, filtration and removal of the solvent in vacuum affords the product; yield: 7 g (100%); m.p. 79–80° (pentane); b.p. 113–114°/14 torr.

Nitrile oxides **50** react regiospecifically with trimethylsilylalkynes **39** to afford the isoxazoles **51**<sup>23,8</sup>.



|   | R <sup>1</sup>   | R <sup>2</sup>                     | Yield [%] |
|---|--|------------------------------------|-----------|
| a | H <sub>3</sub> C   | (H <sub>3</sub> C) <sub>3</sub> Si | 46        |
| b | C <sub>6</sub> H <sub>5</sub>                            | (H <sub>3</sub> C) <sub>3</sub> Si | 44        |
| c | 1,3,5-tri-H <sub>3</sub> C-C <sub>6</sub> H <sub>2</sub> | (H <sub>3</sub> C) <sub>3</sub> Si | 98        |
| d | H <sub>3</sub> C   | H                                  | 69        |
| e | C <sub>6</sub> H <sub>5</sub>                            | H                                  | 62        |
| f | 1,3,5-tri-H <sub>3</sub> C-C <sub>6</sub> H <sub>2</sub> | H                                  | 98        |

The triazolyltrimethylsilanes **53–55** are obtained in good yields via the addition of azides **52** to trimethylsilylalkynes **39**<sup>23,9</sup>.



|   | R <sup>1</sup>                     | R <sup>2</sup>                     | Yield ( <b>53</b> ) [%] | Yield ( <b>54</b> ) [%] | Yield ( <b>55</b> ) [%] |
|---|------------------------------------|------------------------------------|-------------------------|-------------------------|-------------------------|
| a | (H <sub>3</sub> C) <sub>3</sub> Si | (H <sub>3</sub> C) <sub>3</sub> Si | —                       | —                       | 66                      |
| b | (H <sub>3</sub> C) <sub>3</sub> Si | C <sub>6</sub> H <sub>5</sub>      | —                       | —                       | 87                      |
| c | C <sub>6</sub> H <sub>5</sub>      | (H <sub>3</sub> C) <sub>3</sub> Si | 76                      | —                       | —                       |
| d | C <sub>6</sub> H <sub>5</sub>      | C <sub>6</sub> H <sub>5</sub>      | 3                       | 97                      | —                       |
| e | C <sub>6</sub> H <sub>5</sub>      | COOCH <sub>3</sub>                 | —                       | 80                      | —                       |
| f | C <sub>6</sub> H <sub>5</sub>      | COOC <sub>2</sub> H <sub>5</sub>   | —                       | 65                      | —                       |

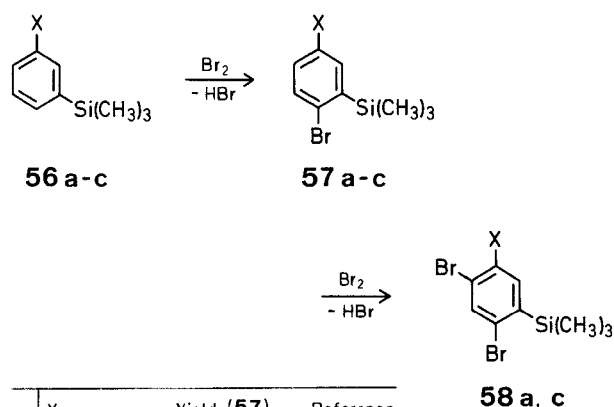
Triazoles of type **54** are also formed in low yields by the addition of trimethylsilyldiazomethane to carbodiimides<sup>24,0</sup>.

## 4. Introduction of Substituents into the Nucleus of Aryl- and Heteroaryltrimethylsilanes

The often rigorous reaction conditions needed for the direct introduction of trimethylsilyl groups into aromatic and heteroaromatic compounds (c.f. Section 2) require that various functional groups be introduced into the nucleus after silylation or subsequently constructed by transformation of substituents already present. Ideally, the trimethylsilyl group plays thereby the role of an inert substituent. With the introduction of electrophiles, the desilylation reactions<sup>3</sup> can dominate over the desired deprotonation reactions, thus affording completely desilylated products. Desilylation is avoided by the use of organometallic derivatives which are always more reactive towards electrophiles than the corresponding hydrogen compounds. In the case of the transformation of substituents attached to the nucleus, reaction conditions have to be chosen to avoid cleavage of the trimethylsilyl groups.

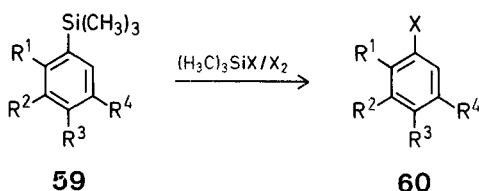
### 4.1. Halogenation

Halodesilylation reactions proceed extremely well; thus the *ipso*-rate factor is 10<sup>8</sup> for the bromination and 10<sup>6</sup> for the chlorination of phenyltrimethylsilane<sup>3</sup>. Consequently, nuclear halogenation reactions without considerable halodesilylation are only possible at strongly activated positions, for example in the *p*- and *o*-positions of *m*-trimethylsilyl-substituted anilines and phenols **56**.



| X                                  | Yield ( <b>57</b> ) [%] | Reference |
|------------------------------------|-------------------------|-----------|
| a OH                               | 83                      | 241, 242  |
| b NHCOCH <sub>3</sub>              | 100                     | 243, 244  |
| c N(CH <sub>3</sub> ) <sub>2</sub> | 86                      | 245, 246  |

The partial halodesilylation of bis[trimethylsilyl]benzenes **59** to the corresponding halophenyltrimethylsilanes **60** is of broader applicability (Table 16).



**Table 16.** Halophenyltrimethylsilanes **60** via Halodesilylation of Bis[trimethylsilyl]benzene Derivatives **59**

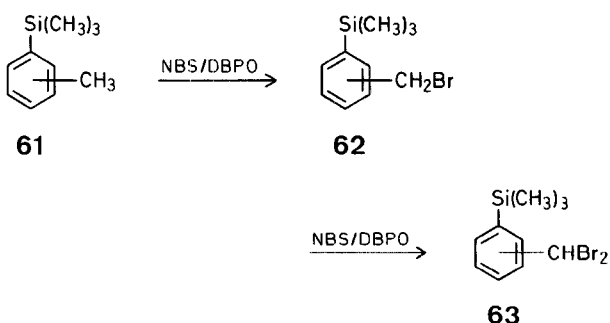
| Substrate <b>59</b>                |                                    | R <sup>3</sup>                     | R <sup>4</sup> | X  | Yield [%] | Reference            |
|------------------------------------|------------------------------------|------------------------------------|----------------|----|-----------|----------------------|
| R <sup>1</sup>                     | R <sup>2</sup>                     |                                    |                |    |           |                      |
| (H <sub>3</sub> C) <sub>3</sub> Si | H                                  | H                                  | H              | J  | 40-95     | 42, 247 <sup>a</sup> |
| H                                  | (H <sub>3</sub> C) <sub>3</sub> Si | H                                  | H              | J  | 85-96     | 247 <sup>a</sup>     |
| H                                  | H                                  | (H <sub>3</sub> C) <sub>3</sub> Si | H              | J  | 82-97     | 247 <sup>a</sup>     |
| (H <sub>3</sub> C) <sub>3</sub> Si | H                                  | H                                  | H              | Br | —         | 142                  |
| (H <sub>3</sub> C) <sub>3</sub> Si | —                                  | (CH <sub>2</sub> ) <sub>2</sub>    | H              | Br | —         | 227                  |
| (H <sub>3</sub> C) <sub>3</sub> Si | H                                  | (CH <sub>2</sub> ) <sub>2</sub>    | —              | Br | —         | 226                  |
| (H <sub>3</sub> C) <sub>3</sub> Si | H                                  | (CH-CH) <sub>2</sub>               | —              | Br | 89        | 228                  |

<sup>a</sup> Also used were J<sub>2</sub>, JCl, and JBr.

### 3-Iodophenyltrimethylsilane<sup>247</sup>:

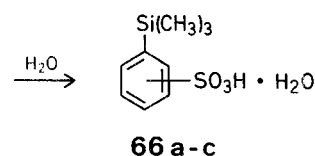
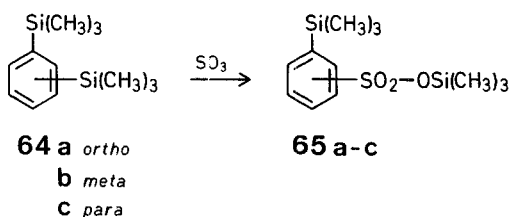
At 0° a solution of iodine bromide (11.4 g, 0.055 mol) in carbon tetrachloride (30 ml) is added dropwise to a solution of 1,3-bis[trimethylsilyl]benzene (11.1 g, 0.05 mol) in carbon tetrachloride (80 ml), the mixture is kept for 1 to 2 h without cooling. Bromotrimethylsilane and carbon tetrachloride are distilled off, the residue is dissolved in ether, washed with 0.3 molar sodium thiosulfate solution (50 ml), then with water, and dried with sodium sulfate. Distillation affords the product; yield: 11.5 g (85%); b.p. 146-150°/30 torr.

Halogenated heteroaryltrimethylsilanes are also obtainable in this way. 4,5-Bis[trimethylsilyl]-3-methylisoxazole undergoes selective bromodesilylation on treatment with bromine only at the 4-position (69%)<sup>238</sup>. Examples for the halogenation of trimethylsilyl-substituted organometallic compounds, which, as expected, do not undergo halodesilylation, have also been described; i.e. the chlorination of 2-lithio-5-trimethylsilylthiophene (45%)<sup>248</sup>, as well as the bromination (33%) and iodination (67%) of 2-lithiophenyltrimethylsilane<sup>126</sup>. In contrast to the reactions at the nucleus, the direct halogenation of side chains proceeds in a free radical manner, thus preventing undesirable halodesilylation. Depending on the reaction conditions, the bromination of the tolyltrimethylsilanes **61** with *N*-bromosuccinimide (NBS)/dibenzoyl peroxide (DBPO) leads to the monobromomethylbenzenes **62** (59-66%) or dibromomethylbenzenes **63** (46-70%)<sup>249, 250</sup>.



## 4.2. Introduction of Sulfur Functions

Aryltrimethylsilanes react with sulfur trioxide or trimethylsilyl chlorosulfonate with insertion of sulfur trioxide into the carbon-silicon bond to yield trimethylsilyl esters of arenesulfonic acids<sup>251</sup>, which can easily be hydrolyzed to the free sulfonic acids. For example, by partial sulfodesilylation of the bis[trimethylsilyl]benzenes **64**, sulfonic acids **66** can be prepared via the isolable trimethylsilyl esters **65** (80-88%)<sup>123, 142, 252, 253</sup>.

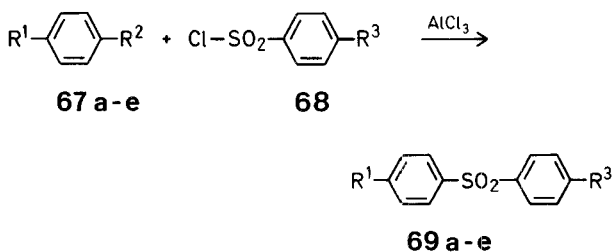


The deactivating trimethylsilyloxysulfonyl group in **65** impedes a further electrophilic attack of sulfur trioxide at the second trimethylsilyl group.

### 4-[Trimethylsilyl]benzenesulfonic Acid Monohydrate (**66c**)<sup>252</sup>:

A solution of sulfur trioxide (4.0 g, 0.05 mol) in carbon tetrachloride (40 ml) is added dropwise, with exclusion of moisture, to a stirred solution of **64c** (17 g, 0.077 mol) in carbon tetrachloride (70 ml) cooled with ice/water. The mixture is heated under reflux for 15 min and then fractionally distilled to give **64c**; yield: 5.1 g (30%); b.p. 79°/2 torr and trimethylsilyl 4-(trimethylsilyl)benzenesulfonate (**65c**); yield: 12.1 g (80% based on **64c** consumed); b.p. 150-151°/2 torr; m.p. 83-86°. Compound **65c** is dissolved in water (15 ml) and after 15 min, water and hexamethyldisiloxane are evaporated and the residue recrystallized from benzene to give **66c**; yield: 2.1 g (85%); m.p. 89-90°.

Trimethylsilyl-substituted diarylsulfones are prepared by either partial sulfonyl desilylation of bis[trimethylsilyl]aromatic compounds **67a-c** using sulfo-



|          | R <sup>1</sup>   | R <sup>2</sup>                     | R <sup>3</sup>                     | Yield [%] |
|----------|--|------------------------------------|------------------------------------|-----------|
| <b>a</b> | (H <sub>3</sub> C) <sub>3</sub> Si                                   | (H <sub>3</sub> C) <sub>3</sub> Si | H                                  | 48        |
| <b>b</b> | (H <sub>3</sub> C) <sub>3</sub> Si                                   | (H <sub>3</sub> C) <sub>3</sub> Si | CH <sub>3</sub>                    | 54        |
| <b>c</b> | 4-(H <sub>3</sub> C) <sub>3</sub> Si-C <sub>6</sub> H <sub>4</sub> - | (H <sub>3</sub> C) <sub>3</sub> Si | H                                  | 63        |
| <b>d</b> | CH <sub>3</sub>  | H                                  | (H <sub>3</sub> C) <sub>3</sub> Si | 76        |
| <b>e</b> | H  | H                                  | (H <sub>3</sub> C) <sub>3</sub> Si | 87        |

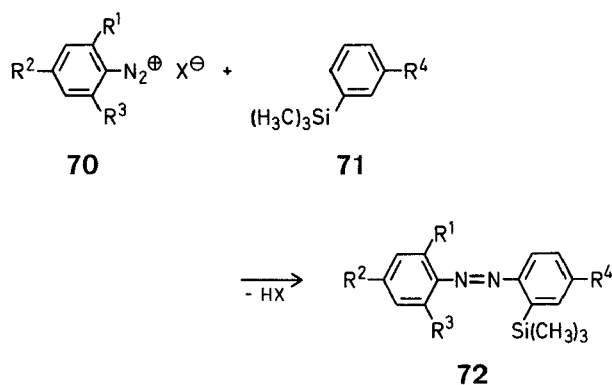


nyl chlorides **68** or by sulfonylation of unsilylated aromatic compounds **67d, e** with trimethylsilyl-substituted sulfonyl chlorides **68** [ $R^3 = \text{Si}(\text{CH}_3)_3$ ]<sup>254</sup>.

Trimethylsilyl-substituted thiophenols (~50%) are formed when the corresponding Grignard or lithium compounds are allowed to react with elemental sulfur<sup>255,256</sup> or with diallyl sulfide<sup>85</sup>.

### 4.3. Introduction of Nitrogen Functions

A number of arenediazonium salts **70** react with derivatives of aniline and phenol **71** ( $R^4 = \text{NR}_2, \text{OH}$ ) carrying trimethylsilyl groups in the *meta*-position, to afford the azo compounds **72** (Table 17).



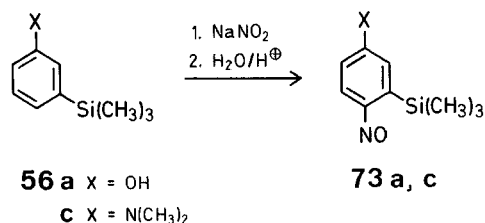
**Table 17.** Trimethylsilyl-Substituted Azo Compounds **72** via Coupling of Diazonium Salts **70** with Aryltrimethylsilanes **71**

| $R^1$                    | $R^2$                    | $R^3$ | $R^4$   | Yield [%] | Reference        |
|--------------------------|--------------------------|-------|---|-----------|------------------|
| H                        | $\text{NO}_2$            | H     | $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$ | 50        | 160              |
| Cl                       | $\text{NO}_2$            | H     | $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$ | 60        | 160              |
| Cl                       | $\text{NO}_2$            | Cl    | $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$ | 60        | 160              |
| $\text{CF}_3$            | $\text{NO}_2$            | H     | $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$ | 50        | 160              |
| $\text{SO}_2\text{CH}_3$ | $\text{NO}_2$            | H     | $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$ | 52        | 160              |
| $\text{SO}_2\text{CH}_3$ | $\text{SO}_2\text{CH}_3$ | H     | $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$ | 34        | 160              |
| H                        | H                        | H     | $\text{N}(\text{CH}_3)_2$                     | 60        | 143, 245         |
| H                        | $\text{NO}_2$            | H     | $\text{N}(\text{CH}_3)_2$                     | 95        | 143, 245         |
| $\text{NO}_2$            | $\text{NO}_2$            | H     | $\text{N}(\text{CH}_3)_2$                     | 36        | 143              |
| Cl                       | $\text{NO}_2$            | H     | $\text{N}(\text{CH}_3)_2$                     | 77        | 143              |
| Cl                       | $\text{NO}_2$            | Cl    | $\text{N}(\text{CH}_3)_2$                     | 66        | 143              |
| $\text{NO}_2$            | $\text{NO}_2$            | Cl    | $\text{N}(\text{CH}_3)_2$                     | 35        | 143              |
| $\text{CF}_3$            | $\text{NO}_2$            | H     | $\text{N}(\text{CH}_3)_2$                     | 83        | 143              |
| $\text{SO}_2\text{CH}_3$ | $\text{NO}_2$            | H     | $\text{N}(\text{CH}_3)_2$                     | 69        | 143              |
| $\text{SO}_2\text{CH}_3$ | $\text{SO}_2\text{CH}_3$ | H     | $\text{N}(\text{CH}_3)_2$                     | 51        | 143              |
| OH                       | $\text{NO}_2$            | H     | $\text{N}(\text{CH}_3)_2$                     | 14        | 143              |
| H                        | $\text{SO}_3\text{H}$    | H     | $\text{N}(\text{CH}_3)_2$                     | 87        | 143              |
| H                        | $\text{SO}_2\text{NH}_2$ | H     | $\text{N}(\text{CH}_3)_2$                     | 75        | 143              |
| COOH                     | H                        | H     | $\text{N}(\text{CH}_3)_2$                     | 53        | 143              |
| H                        | COOH                     | H     | $\text{N}(\text{CH}_3)_2$                     | 65        | 143 <sup>a</sup> |
| H                        | $\text{SO}_3\text{H}$    | H     | OH  | —         | 257              |

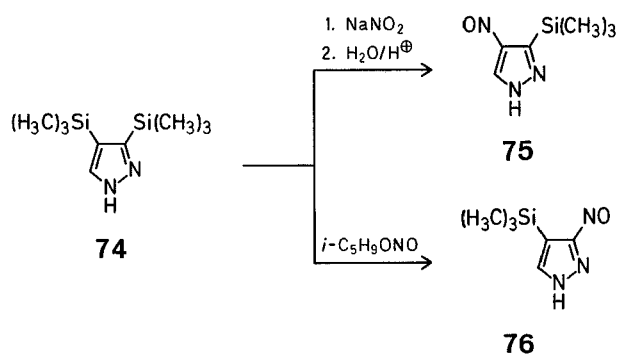
<sup>a</sup> Includes azo derivatives of 2-naphthol.

As expected, *p*-trimethylsilyl-substituted anilines or phenols undergo diazodesilylation<sup>143</sup>. In contrast, 2-dimethylaminophenyltrimethylsilane does not react with diazonium salts due to steric hindrance<sup>143</sup>. However, 2-trimethylsilylphenol couples in the 4-position<sup>258</sup>. 2- or 4-trimethylsilyl-substituted azo com-

pounds can be obtained without desilylation occurring if the trimethylsilyl group is located on the diazonium component **70**<sup>259</sup>. A nitrosation of aryltrimethylsilanes while maintaining the carbon-silicon bond intact is also possible, but only with strongly activated anilines<sup>245</sup> or phenols<sup>257</sup> of type **56**.



The nitroso group has to be introduced by nitrosodesilylation reactions into less activated aryltrimethylsilanes, for example, to produce 3- or 4-nitrosophenyltrimethylsilane (50%)<sup>260</sup>. Selective nitrosodesilylation reactions were carried out with 3,4-bis[trimethylsilyl]pyrazole (**74**) leading to **75** (39–77%) or **76** (36%)<sup>261</sup>.

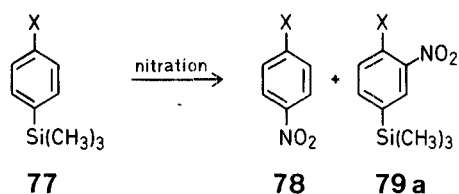


Sulfuric acid/nitric acid mixtures cannot be used for the nitration of aryltrimethylsilanes because of the ease of protodesilylation. In weakly acidic medium, phenyltrimethylsilane reacts with nitrating agents such as nitric acid/acetic anhydride, copper nitrate/acetic anhydride, or others<sup>102,262–265</sup> predominantly maintaining the carbon-silicon bond intact to form a mixture of *o*-, *m*-, and *p*-nitrophenyltrimethylsilanes. The somewhat favoured formation of the *m*-product is a basis for conclusions about the directive effect of the trimethylsilyl group<sup>266</sup>. For the specific preparation of certain isomers it is more convenient to apply partial nitrosodesilylation of the corresponding bis[trimethylsilyl]benzenes **64** using nitric acid in acetic anhydride [*o* (90%)<sup>142</sup>, *m* (69%)<sup>85,265</sup>, *p* (82%)<sup>267</sup>]. In contrast to earlier presumptions<sup>6,28</sup> these reactions do not seem to be explosive<sup>268</sup>.

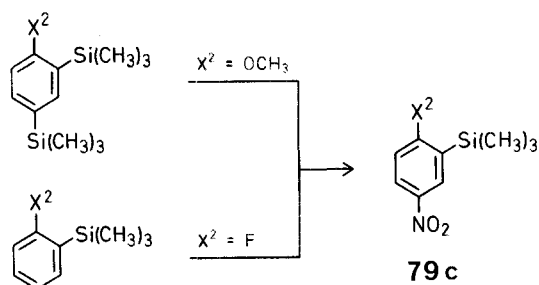
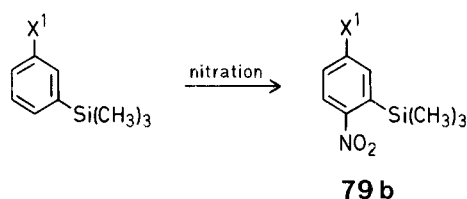
#### 2-Nitrophenyltrimethylsilane<sup>142</sup>:

A solution of nitric acid (70%; 6.3 g, 0.07 mol) in acetic anhydride (30 g) is added slowly to a solution of 1,2-bis[trimethylsilyl]benzene (4.5 g, 0.02 mol) in acetic acid. The mixture is kept at 100° for 6 h, then cooled, and added to 0.4 molar aqueous sodium hydroxide solution (400 ml). Ether extraction, followed by washing, drying with sodium sulfate, and fractionation gives the product; yield: 3.5 g (90%); b.p. 98°/2.3 torr;  $n_D^{25}$ : 1.5271.

Depending on substituents X, *p*-substituted aryltrimethylsilanes **77** undergo nitrodesilylation to form **78** or normal nitration to form **79a**.



| X                   | Yield ( <b>78</b> ) [%] | Yield ( <b>79</b> ) [%] | Reference |
|---------------------|-------------------------|-------------------------|-----------|
| NHCOCH <sub>3</sub> | 29                      | 51                      | 269       |
| OCOCH <sub>3</sub>  | 80                      | —                       | 270       |
| OCH <sub>3</sub>    | 82                      | —                       | 6         |
| CH <sub>3</sub>     | —                       | 55                      | 263       |
| F                   | 67                      | —                       | 72        |
| F                   | —                       | 16                      | 78        |
| Cl                  | —                       | —                       | 271       |



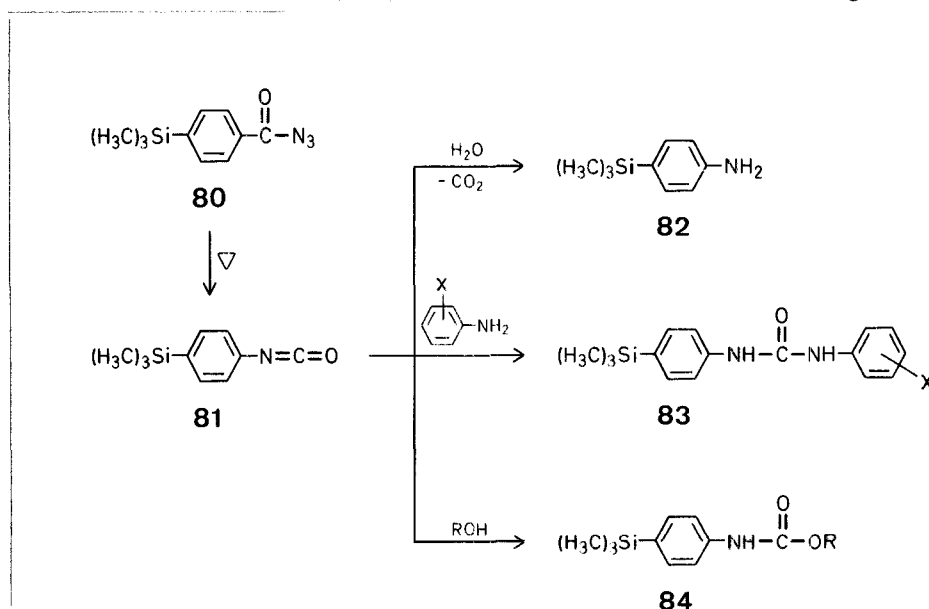
Reactions of the *m*-isomers lead to the products of normal nitration **79b** [X<sup>1</sup> = N(CH<sub>3</sub>)<sub>2</sub> (40%)<sup>245</sup>, OCH<sub>3</sub> (81%)<sup>6</sup>, F (65%)<sup>78</sup>, Cl (80%)<sup>271</sup>]. 3-Trimethylsilylacetyl-anilide is predominantly nitrated *ortho* to the acetyl-amino group (70%)<sup>243</sup>.

The preparation of the silanes **79c** [X<sup>2</sup> = OCH<sub>3</sub> (74%)<sup>207</sup>, F (19%)<sup>78</sup>] results from nitrodesilylation or nitration, respectively. The nitration of 3-trimethylsilylpyrazole affords 4-nitro-3-trimethylsilylpyrazole (94%)<sup>235</sup>. The introduction of amino groups into the aromatic nucleus is usually done in a nucleophilic manner or via rearrangement reactions. Thus, in the reaction of 4-bromophenyltrimethylsilane with lithium dimethylamide in ether – via the aryne intermediate – 3-dimethylaminophenyltrimethylsilane is the main product (56%)<sup>145</sup>.

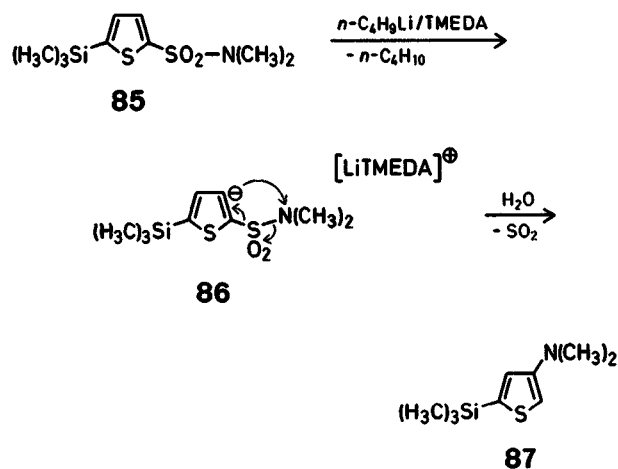
The application of rearrangement reactions to introduce amino and functionalized amino groups into the nucleus of aryl- and heteroaryltrimethylsilanes can be exemplified by the Hofmann-rearrangement of 3-trimethylsilylbenzamide<sup>144</sup> and 3-trimethylsilylisonicotinic acid amide<sup>154</sup> to give the amines, the Curtius rearrangement of 4-trimethylsilylbenzoyl azide **80** to give the isocyanate **81**<sup>272</sup>, as well as the Beckmann reaction of the 4-trimethylsilylacetophenone oxime with phosphorus pentachloride or thionyl chloride to give the corresponding acetanilide (87%)<sup>273</sup>.

The reaction of **81** with water, after elimination of carbon dioxide, affords the amine **82**. Reaction of **81** with anilines affords the diarylureas **83** [X = H, 2-CH<sub>3</sub>, 2-OCH<sub>3</sub>, 4-OC<sub>2</sub>H<sub>5</sub>, 2-Cl, 4-Cl, 2,4-di-Cl, 4-(CH<sub>3</sub>)<sub>3</sub>Si] and with alcohols, urethanes **84** (R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, *n*-C<sub>3</sub>H<sub>7</sub>, *n*-C<sub>4</sub>H<sub>9</sub>, C<sub>5</sub>H<sub>11</sub>, C<sub>6</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>) are formed<sup>272</sup>.

Compound **81** eliminates carbon dioxide when heated (5 h, 130–150°) in the presence of 5-methyl-5*H*-dibenzophosphole and gives the carbodiimide (84%)<sup>274</sup>. The sulfonamide **85** can be rearranged us-



ing butyllithium via the anion **86** to yield **87** (93%) with cleavage of sulfur dioxide<sup>176</sup>.

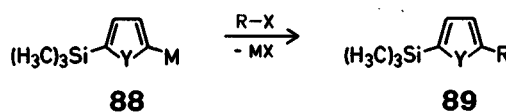


#### 4.4. Introduction of Phosphorus Functions

In order to introduce phosphorus substituents into aryltrimethylsilanes, it is necessary to use organometallic compounds, because otherwise phosphodesilylation<sup>275</sup> occurs under the conditions of electrophilic phosphorylation (Table 18).

#### 4.5. Alkylation and Hydroxyalkylation

Since aryltrimethylsilanes undergo alkyldesilylation<sup>3,279</sup> under Friedel-Crafts conditions only, the partial alkyldesilylation of poly[trimethylsilyl]benzenes can lead to the desired compounds. In this manner the reaction of 1,2-bis[trimethylsilyl]benzene (**64a**) with *t*-butyl chloride/aluminum trichloride gives 2-*t*-butylphenyltrimethylsilane<sup>142</sup>. Again, alkyldesilylation can be avoided by the use of the corresponding organometallic compounds **88**. By reaction with alkylating agents  $\text{R-X}$ , an access to various alkylated compounds **89** is provided (Table 19).



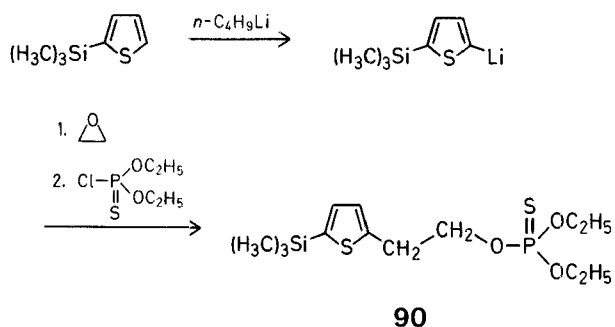
The biologically active thiophene derivative **90** is obtained by alkylation of the 2-lithio-5-trimethylsilylthiophene with oxirane and subsequent phosphorylation (51%)<sup>179</sup>.

Table 18. Phosphorus-Substituted Aryl- and Heteroaryltrimethylsilanes via Trimethylsilyl-Substituted Organometallic Compounds

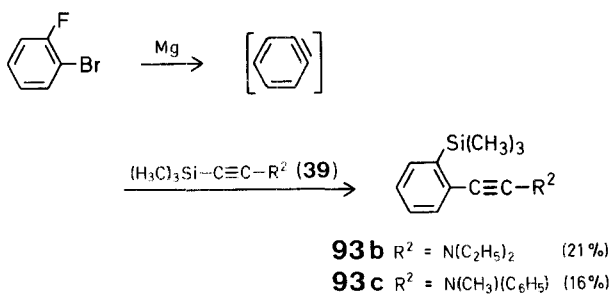
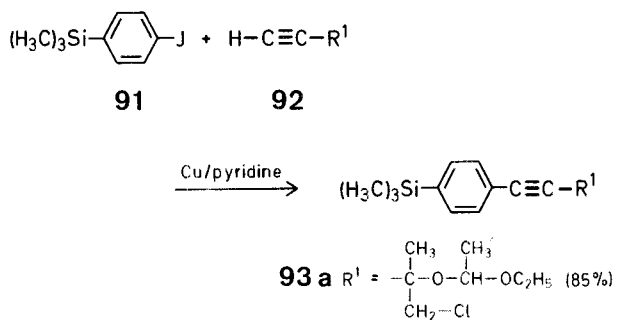
| Substrate   | Phosphorylating Agent               | Product   | Yield [%] | Reference |
|---|-------------------------------------|---|-----------|-----------|
| $(\text{H}_3\text{C})_3\text{Si-C}_6\text{H}_4\text{-MgBr}$ | $\text{PCl}_3$                      | $[(\text{H}_3\text{C})_3\text{Si-C}_6\text{H}_4]_3\text{P}$                     | 35        | 276       |
| $(\text{H}_3\text{C})_3\text{Si-C}_6\text{H}_4\text{-MgBr}$ | $\text{PCl}_5$                      | $[(\text{H}_3\text{C})_3\text{Si-C}_6\text{H}_4]_3\text{P}$                     | 45        | 276       |
| $(\text{H}_3\text{C})_3\text{Si-C}_6\text{H}_4\text{-MgBr}$ | $\text{POCl}_3$                     | $[(\text{H}_3\text{C})_3\text{Si-C}_6\text{H}_4]_3\text{P=O}$                   | 30        | 276       |
| $(\text{H}_3\text{C})_3\text{Si-C}_6\text{H}_4\text{-MgCl}$ | $\text{Cl-P(=O)(OC}_2\text{H}_5)_2$ | $(\text{H}_3\text{C})_3\text{Si-C}_6\text{H}_4\text{-P(=O)(OC}_2\text{H}_5)_2$  | 60        | 277       |
| $(\text{H}_3\text{C})_3\text{Si-C}_6\text{H}_4\text{-MgCl}$ | $\text{Cl-P(=O)(OC}_2\text{H}_5)_2$ | $(\text{H}_3\text{C})_3\text{Si-C}_6\text{H}_4\text{-P(=O)(OC}_2\text{H}_5)_2$  | 60        | 277       |
| $(\text{H}_3\text{C})_3\text{Si-C}_6\text{H}_4\text{-MgCl}$ | $\text{Cl-P(=O)(C}_2\text{H}_5)_2$  | $(\text{H}_3\text{C})_3\text{Si-C}_6\text{H}_4\text{-P(=O)(C}_2\text{H}_5)_2$   | 58        | 278       |
| $(\text{H}_3\text{C})_3\text{Si-C}_6\text{H}_4\text{-MgCl}$ | $\text{Cl-P(=O)(C}_2\text{H}_5)_2$  | $(\text{H}_3\text{C})_3\text{Si-C}_6\text{H}_4\text{-P(=O)(C}_2\text{H}_5)_2$   | 58        | 278       |
| $(\text{H}_3\text{C})_3\text{Si-C}_4\text{H}_3\text{O-Li}$  | $\text{Cl-P(=O)(OC}_2\text{H}_5)_2$ | $(\text{H}_3\text{C})_3\text{Si-C}_4\text{H}_3\text{O-P(=O)(OC}_2\text{H}_5)_2$ | 56        | 179       |
| $(\text{H}_3\text{C})_3\text{Si-C}_4\text{H}_3\text{S-Li}$  | $\text{Cl-P(=O)(OC}_2\text{H}_5)_2$ | $(\text{H}_3\text{C})_3\text{Si-C}_4\text{H}_3\text{S-P(=O)(OC}_2\text{H}_5)_2$ | 46        | 179       |
| $(\text{H}_3\text{C})_3\text{Si-C}_4\text{H}_3\text{S-Li}$  | $\text{Cl-P(=O)(OCH}_3)_2$          | $(\text{H}_3\text{C})_3\text{Si-C}_4\text{H}_3\text{S-P(=O)(OCH}_3)_2$          | 66        | 179       |
| $(\text{H}_3\text{C})_3\text{Si-C}_4\text{H}_3\text{S-Li}$  | $\text{Cl-P(=O)(OC}_2\text{H}_5)_2$ | $(\text{H}_3\text{C})_3\text{Si-C}_4\text{H}_3\text{S-P(=O)(OC}_2\text{H}_5)_2$ | 31        | 179       |

**Table 19.** Alkylation of Aryl- and Heteroaryltrimethylsilanes via Organometallic Derivatives **88**

| Substrate <b>88</b><br>Y | M    | R X                   | Yield [%] | Reference |
|--------------------------|------|-----------------------|-----------|-----------|
| -CH=CH-                  | MgBr |                       | —         | 280       |
| -CH=CH-                  | MgBr |                       | 15        | 281       |
| -CH=CH-                  | Li   | F <sub>2</sub> C=CF-F | 32        | 282       |
| S                        | Li   |                       | 4         | 283       |
| S                        | Li   |                       | 50        | 175       |
| S                        | Li   |                       | 29        | 248       |

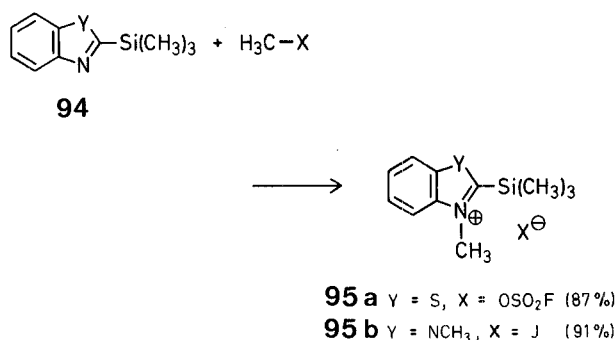


Alkyne-substituted aryltrimethylsilanes **93** can be prepared by coupling reactions of **91** with acetylenes **92**<sup>284</sup>, as well as by addition of trimethylsilylalkynes **39** to benzene<sup>163</sup>.



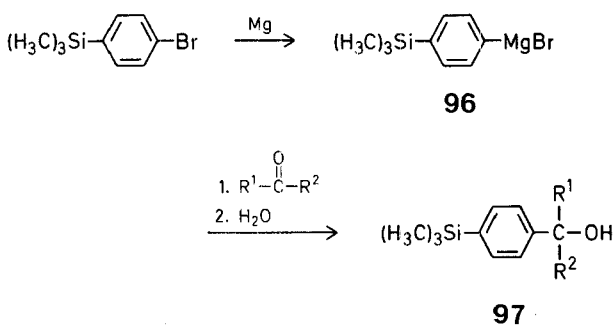
Pentafluorophenyltrimethylsilane can be alkylated with *n*-butyllithium in the 4-position as the result of direct nucleophilic attack<sup>198</sup>.

Alkylation of heteroaryltrimethylsilanes containing nitrogen-hydrogen bonds leads to the *N*-alkylated derivatives<sup>234</sup> and from compounds **94**, salts **95** are obtained<sup>182,184</sup>.



2-Pyridyltrimethylsilane was also converted into the corresponding quaternary iodide (91%)<sup>51</sup>.

The free radical arylation of phenyltrimethylsilane induced by dibenzoyl peroxide gives a mixture of the isomeric trimethylsilyldiphenyls (overall yield 20%)<sup>285</sup>. Hydroxyalkylation of aryltrimethylsilanes with aldehydes in the presence of aluminum trichloride always leads to mixtures of isomers<sup>286</sup>. Organometallic derivatives **96**, however, react with aldehydes and ketones specifically to give the corresponding alcohols **97** (Table 20).

**Table 20.** Benzyl Alcohols **97** via Reactions of Grignard Compounds **96** with Aldehydes or Ketones

| R <sup>1</sup>                | R <sup>2</sup>  | Yield [%] | Reference              |
|-------------------------------|-----------------|-----------|------------------------|
| CH <sub>3</sub>               | H               | 33-50     | 65, 169, 281, 287, 288 |
| CH <sub>3</sub>               | CH <sub>3</sub> | 42-49     | 281, 288, 289, 290     |
| C <sub>6</sub> H <sub>5</sub> | H               | 20-52     | 65, 212                |

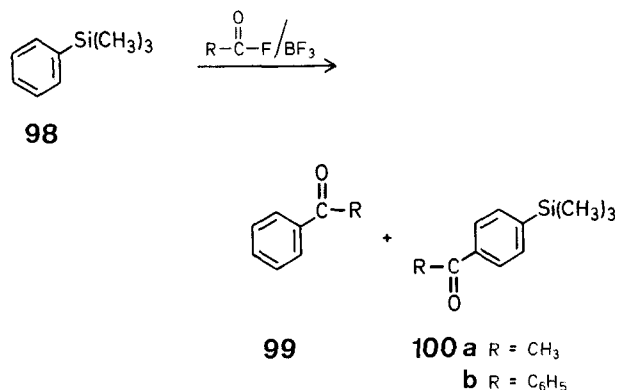
Analogous reactions of 2-lithio-5-trimethylsilylthiophene with benzaldehyde (yield: 30%)<sup>291</sup> as well as of the 5,8-dilithio adduct of 1-naphthyltrimethylsilane with aliphatic aldehydes CH<sub>3</sub>(CH<sub>2</sub>)<sub>n</sub>CHO (n=0, 1, 2, 3; yields: 37-46%)<sup>39</sup> have been described.

#### 4.6. Acylation

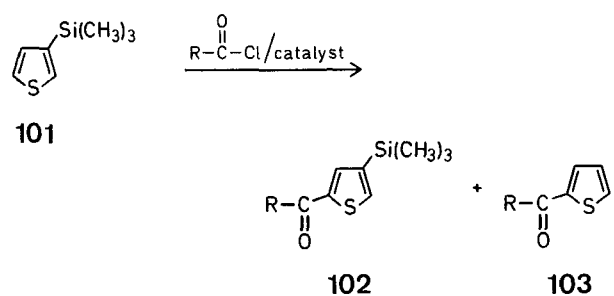
Normal acylation competes with acyldesilylation in the Friedel-Crafts acylation of aryltrimethylsilanes. Thus, acyldesilylation of phenyltrimethylsilane (**98**)

with acetyl chloride/aluminum trichloride is greatly favoured over the normal C—H acylation by an *ipso*-rate factor<sup>3,279</sup> of  $10^3$ – $10^4$ .

With acyl fluorides/boron trifluoride, however, both reaction pathways seem to take place at a comparable rate yielding a mixture of **99** and **100**<sup>65,292</sup>.



Normal acylation is favoured when strong substituent effects counteract the *ipso*-directive effect of the trimethylsilyl group. Thus, 2- and 3-methoxyphenyltrimethylsilane are always acylated *para* to the methoxy group<sup>51, 258, 263</sup> and do not undergo acyldesilylation as was earlier reported<sup>279</sup>. The relations with 3-thienyltrimethylsilane (**101**) are similar. Compound **101** exclusively reacts at the position that favours an electrophilic attack to yield **102** (R = CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>; using tin(IV) chloride titanium(IV) chloride, aluminum chloride as catalysts; yield: 14–52%)<sup>51</sup>. The mineral acid emerging from normal acylation, in the presence of the catalyst causes protodesilylation of still unreacted **101** forming thiophene, which is subsequently acylated to yield **103** (24–59%). This side reaction has not been seriously taken into account in most of the earlier investigations.



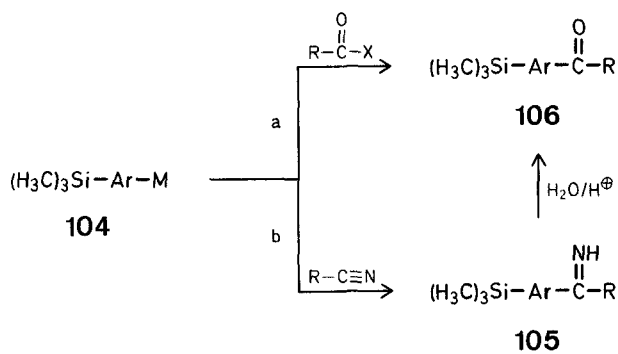
The acylations of 2-thienyltrimethylsilane [acetyl chloride/titanium(IV) chloride (42%)<sup>51</sup>, acetic anhydride/iodine (13%)<sup>293</sup>, benzoyl chloride (17%)<sup>294</sup>], 2-furyltrimethylsilane [acetic anhydride/iodine (25%)<sup>293</sup>], and *N*-methyl-2-pyrrolyltrimethylsilane [phthalic anhydride (55%)<sup>294</sup>] lead to the 5-acyl-2-trimethylsilyl compounds. The only moderate yields indicate that side reactions, involving acid formed by acylation, also take place in these cases. The partial desilylation of poly[trimethylsilyl]aromatic compounds provides a convenient way to prepare acylphenyltrimethylsilanes. Since the reactivity of the

mono-acylated compounds is significantly reduced no further reaction takes place<sup>142</sup>.

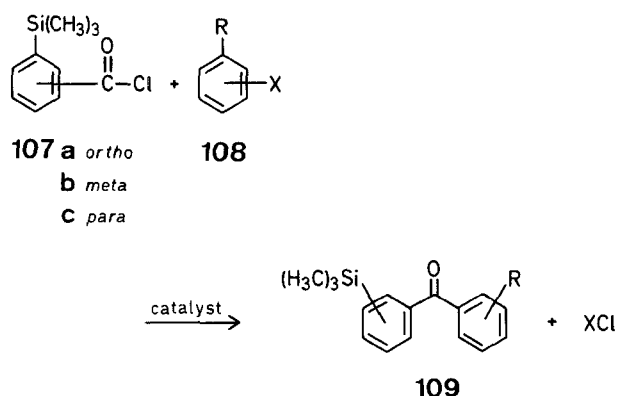
#### 2-Acetylphenyltrimethylsilane<sup>142</sup>:

Acetyl chloride (2.3 g, 0.03 mol) in carbon disulfide (15 ml) is added to a stirred, ice-cooled suspension of aluminum chloride (4.0 g) in carbon disulfide (50 ml) containing 1,2-bis[trimethylsilyl]benzene (6.6 g, 0.03 mol). The mixture is heated under reflux for 1 h, most of the solvent is distilled off, and the residue is added to ice/water (100 ml). Benzene extraction followed by washing, drying with sodium sulfate, and fractionation gives the product; yield: 2.8 g (50%); b.p. 88°/3 torr; n<sub>D</sub><sup>25</sup> 1.5181.

The unwanted side-reaction, acyldesilylation, in the preparation of acylaryl- and -heteroaryltrimethylsilanes can be completely avoided by using the reactive organometallic derivatives **104**. In this case, in addition to the usual acylating agents (i.e. acyl halides or anhydrides), which directly affords ketones **106** (route a), nitriles also can be used. Primarily, the imino derivatives **105** are formed (route b), which after hydrolysis give the ketones **106** (Table 21).



To obtain acylphenyltrimethylsilanes **109**, the trimethylsilyl group can also be introduced by the acylating agent **107**, generally involving Friedel-Crafts catalysts (Table 22).



Trimethylsilyl-substituted alkyl aryl ketones are obtained by addition of aliphatic Grignard compounds RMgX (R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>11</sub>, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>) to 4-cyanophenyltrimethylsilane<sup>296</sup>.

The formylation of aromatic compounds is a special acylation reaction. Reactive aryltrimethylsilanes undergo direct formylation according to Reimer-Tiemann<sup>257, 270, 258</sup> as well as Vilsmeier<sup>245</sup>. In general, tri-

**Table 21.** Acylaryl- and Acylheteroaryltrimethylsilanes **106** via Acylation of Organometallic Compounds **104**

| Substrate <b>104</b> | Route | Acylating agent | Product type                                      | Yield [%] | References |
|----------------------|-------|-----------------|---|-----------|------------|
|                      | b     |                 | <b>106</b>  | 82        | 168        |
|                      | b     |                 | <b>106</b>  | 64        | 166        |
|                      | b     |                 | <b>106</b>  | 33        | 168        |
|                      | b     |                 | <b>105</b>  | 75        | 248        |
|                      | b     |                 | <b>105</b>  | 51        | 248        |
|                      | b     |                 | <b>105</b>  | 54        | 248        |
|                      | b     |                 | <b>105</b>  | 30        | 248        |
|                      | b     |                 | <b>105</b>  | 58        | 248        |
|                      | a     |                 | <b>106</b> (R =                                   | 33        | 295        |
|                      | a     |                 | <b>106</b> (R = H <sub>3</sub> C)                 | 39        | 295        |
|                      | a     |                 | <b>106</b> (R = C <sub>2</sub> H <sub>5</sub> )   | 44        | 295        |
|                      | a     |                 | <b>106</b> (R = n-C <sub>3</sub> H <sub>7</sub> ) | 31        | 295        |
|                      | a     |                 | <b>106</b> (R = H <sub>3</sub> C)                 | 41        | 207        |

**Table 22.** Benzoylaryltrimethylsilanes **109** via Benzoylation with Trimethylsilyl-Substituted Benzoyl Chlorides **107<sup>a</sup>**

| Reactants <b>107</b> <b>108</b> | Catalyst          | R in <b>109</b>                      | Yield [%] | Reference |
|---------------------------------|-------------------|--------------------------------------|-----------|-----------|
|                                 | —                 | 4-H <sub>3</sub> CO                  | —         | 168       |
|                                 | —                 | 4-H <sub>3</sub> C                   | —         | 168       |
|                                 | AlCl <sub>3</sub> | 4-H <sub>3</sub> C                   | 66        | 168       |
|                                 | SnCl <sub>2</sub> | 4-H <sub>3</sub> CO                  | 80        | 168       |
|                                 | AlCl <sub>3</sub> | 4-H <sub>3</sub> C                   | 43        | 168       |
|                                 | AlCl <sub>3</sub> | 4-Cl-C(=O)-                          | 33        | 279       |
|                                 | AlCl <sub>3</sub> | 3-H <sub>3</sub> C                   | 40        | 279       |
|                                 | AlCl <sub>3</sub> | 4-(H <sub>3</sub> C) <sub>3</sub> Si | 75        | 279       |

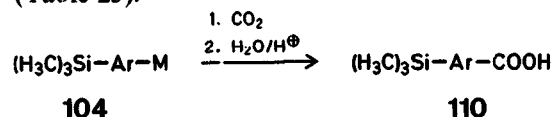
<sup>a</sup> 2-Thienyltrimethylsilane was also acylated with **107c** in this way (32%)<sup>279</sup>.

methylsilyl-substituted aromatic Grignard compounds can be converted to silylated aromatic aldehydes by use of formic acid orthoesters<sup>62,297</sup>, dimethylformamide<sup>175</sup>, or formic esters<sup>298</sup>.

The direct introduction of cyano groups into aryltrimethylsilanes is rather difficult to achieve. The use of cyanogen chloride/aluminum trichloride predominantly results in desilylation<sup>299</sup> and use of copper(I) cyanide and aryl bromides provides low yields (12%) even when vigorous conditions are applied<sup>296</sup>. Therefore the elimination of water from acyl amides using phosphoryl chloride is the preferred method (86%)<sup>204</sup> to obtain cyanophenyltrimethylsilanes.

#### 4.7. Carboxylation

The carboxylation of aryl- and heteroaryltrimethylsilanes is almost exclusively achieved by reaction of organometallic compounds **104** with carbon dioxide (Table 23).



**Table 23.** Trimethylsilyl-Substituted Aromatic and Heteroaromatic Carboxylic Acids **110** via Carboxylation of Organometallic Compounds **104**

| Substrate <b>104</b> | Yield [%] | Reference    | Substrate <b>104</b> | Yield [%] | Reference |
|----------------------|-----------|--------------|----------------------|-----------|-----------|
|                      | 60        | 142, 168     |                      | —         | 171       |
|                      | 48        | 85, 99, 144  |                      | 62        | 293       |
|                      | 38-66     | 99, 168, 300 |                      | 62*       | 293       |
|                      | —         | 207          |                      | 48        | 301       |
|                      | 40        | 157          |                      | 10        | 176       |
|                      | —         | 171          |                      |           |           |

\* Treatment with ethyl chloroformate affords the corresponding furan carboxylic ester (59%)<sup>302</sup>.

**Table 24.** Silylation of Organometallic Derivatives of Aryl- and Heteroaryltrimethylsilanes

| Organometallic Derivative | Silylating Agent   | Product   | Yield [%] | Reference |
|---------------------------|--|---|-----------|-----------|
|                           |  |   | 52        | 303*      |
|                           | $\text{H}_3\text{C}-\text{Si}(\text{OC}_2\text{H}_5)_3$                        |   | 57        | 252       |
|                           | $(\text{C}_6\text{H}_5)_2\text{SiCl}_2$  |   | 86        | 140       |
|                           | $\text{SiCl}_4$  | $[(\text{H}_3\text{C})_3\text{Si}-\text{C}_6\text{H}_4]_4\text{Si}$ | 77        | 140       |
|                           | $(\text{H}_3\text{C})_2\text{SiCl}_2$  |   | 41        | 167       |
|                           | $(\text{H}_3\text{C})_2\text{Si}(\text{Cl})-\text{O}-\text{Si}(\text{CH}_3)_2$ |   | 20        | 167       |
|                           | $\text{C}_6\text{H}_5-\text{Si}(\text{CH}_3)_2-\text{Cl}$                      |   | 30        | 291       |
|                           | $(\text{H}_3\text{C})_3\text{SiCl}$  |   | 17        | 291       |
|                           | $\text{C}_6\text{H}_5-\text{Si}(\text{CH}_3)_2-\text{Cl}$                      |   | 17        | 291       |
|                           | $\text{Na/F}-\text{Si}(\text{C}_6\text{H}_5)_3$                                |   | 75        | 252       |

\* Further trimethylsilyl-substituted oligomers are listed here.

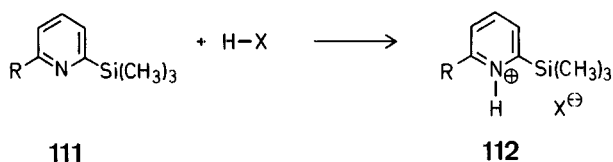
#### 4.8. Silylation

The stability of carbon-silicon bonds towards organometallic compounds makes it possible to introduce further silyl groups into aryl- and heteroaryltrimethylsilanes. The hereby applied methods are not different from those used to introduce the first trimethylsilyl group (cf. Section 2.3.) (Table 24).

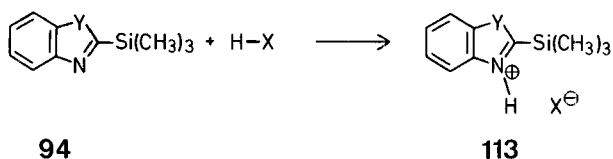
#### 4.9. Protonation

Protonation of aryl- and heteroaryltrimethylsilanes leads to the formation of salts, protodesilylation, or replacement of other substituents by hydrogen, according to the substrate and the reaction conditions.

Basic heteroaryltrimethylsilanes **111** or **94** react with acids to form salts **112** or **113**.

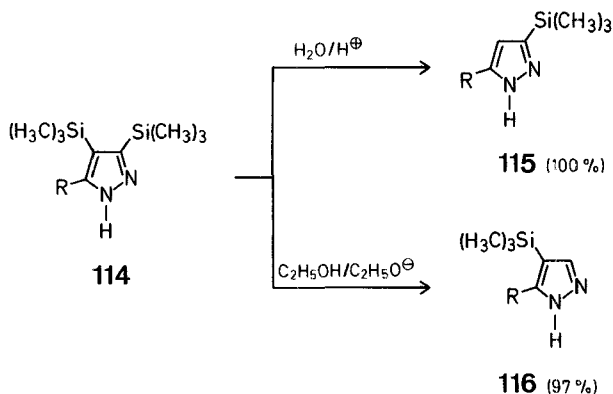


R = H; X = Cl, Br, J, BF<sub>4</sub><sup>-</sup>  
R = H, Br, Si(CH<sub>3</sub>)<sub>3</sub>; X = GeCl<sub>3</sub><sup>-</sup>



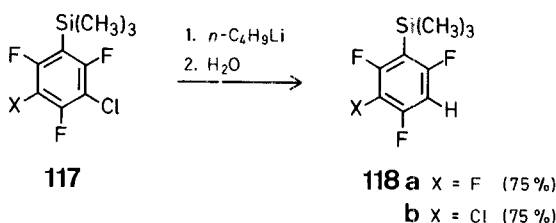
Y = S; X = Cl, J<sup>184</sup>  
Y = NCH<sub>3</sub>; X = Cl<sup>182</sup>  
Y = S; X = GeCl<sub>3</sub><sup>304</sup>

3,4-Bis[trimethylsilyl]pyrazole (**114**; R = H) can be converted quantitatively into its nitrate or hydrochloride by treatment with concentrated acids<sup>305</sup>. However, in sulfuric acid/ice, protodesilylation occurs. Thus, the trimethylsilyl group of **114** (R = H, COOC<sub>2</sub>H<sub>5</sub>) can selectively be removed from position 3- or 4-, according to the reaction conditions<sup>235</sup>.



4,5-Bis[trimethylsilyl]-3-methylisoxazole behaves analogously<sup>238</sup>. 3,5-Bis[trimethylsilyl]-1-methylimid-

azole is smoothly hydrolyzed in a water/dichloromethane mixture to give 1-methyl-5-(trimethylsilyl)imidazole (90%)<sup>182</sup>. Halide substituents in aryltrimethylsilanes **117** can be replaced by hydrogen via the organometallic intermediate without reaction occurring at the trimethylsilyl group<sup>171</sup>.

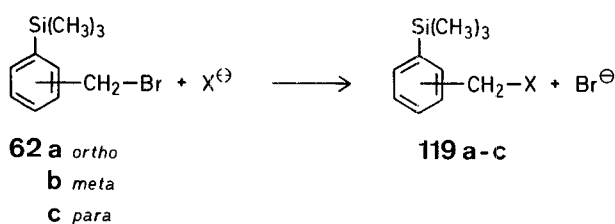


### 5. Transformation of Substituents in Aryl- and Heteroaryltrimethylsilanes

Aside from the substitution reactions at the nucleus of aryl- and heteroaryltrimethylsilanes, the transformation and functionalization of substituents, attached to the silylated ring, is an important method for the preparation of some aryltrimethylsilanes. Hereby, it is important to choose reaction conditions that do not permit desilylation reactions.

#### 5.1. Nucleophilic Exchange of Halides

Benzyl bromides **62**, readily available by radical halogenation of tolyltrimethylsilanes (cf. Section 4.1.), easily react with nucleophiles (X) with substitution of bromide.



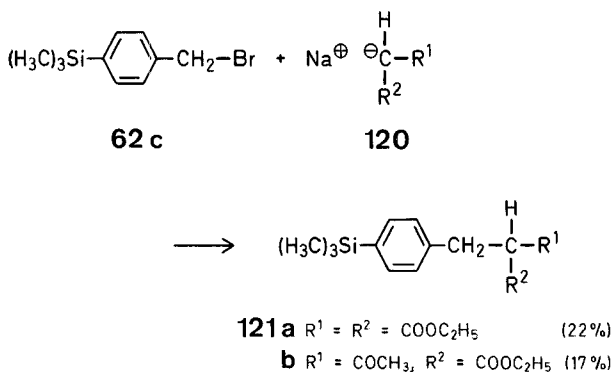
Thus, alcohols **119e** (X = OH)<sup>306</sup> are formed with hydroxide ions as well as ethers **119c** (X = OCH<sub>3</sub>, OC<sub>2</sub>H<sub>5</sub>, OC<sub>6</sub>H<sub>5</sub>)<sup>306</sup> with alcoholates, and esters **119a-c** (X = OCOCH<sub>3</sub>)<sup>250</sup> with carboxylates. The intramolecular substitution of chlorohydrins leads to oxiranes<sup>284</sup>. With sodium hydrogen sulfide, thiophenols **119c** (X = SH)<sup>306</sup> and with sodium methyl mercaptide, thioethers **119c** (X = SCH<sub>3</sub>)<sup>306</sup> are obtained. Amino groups [X = NHCH<sub>3</sub>, N(CH<sub>3</sub>)<sub>2</sub>] can be introduced by using amines or lithium amides<sup>306,278</sup>. Diethyl (trimethylsilyl)-phenylmethanephosphonates **119b, c** [X = P(O)(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>] arise from the reaction of **62b, c** with sodium diethyl phosphite<sup>227</sup>.

Cyanomethylphenyltrimethylsilanes **119** (X = CN), important for further conversions, can be prepared in good yields by reacting **62** with cyanide ions<sup>306-308</sup>. Trimethylsilyl-substituted phenylacetic acids, obtained by saponification of nitriles **119a-c**



(X = CN) in yields of 80–90%<sup>306,307</sup>, afford the methyl esters when treated with diazomethane<sup>306</sup>. The corresponding amide is obtained in 83% yield<sup>163</sup> from the reaction of *N,N*-diethyl[2-trimethylsilylphenylethynyl]amine with hydrogen chloride/ether.

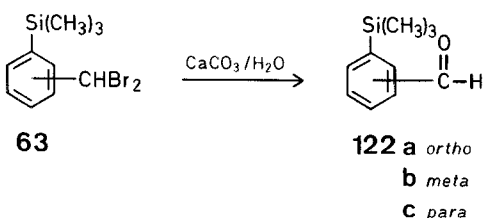
The acidic  $\alpha$ -C—H bond of 4-cyanomethylphenyltrimethylsilane **119c** (X = CN) can be methylated with sodium amide/methyl iodide (80%) or acylated with sodium ethoxide/ethyl acetate<sup>307</sup>. Salts of C—H acidic compounds **120** have been used as C-nucleophiles to afford compounds **121**<sup>308</sup>.



The conversion of the benzyl bromide **62c** to the Grignard derivative **119c** (X = MgBr) and subsequent treatment with sulfur chloride leads to the sulfonyl chloride **119c** (X = SO<sub>2</sub>Cl)<sup>309</sup>.

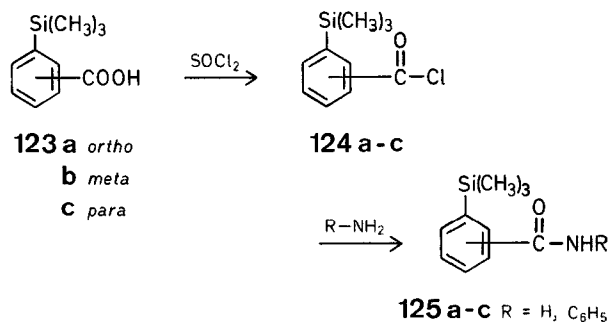
Substitution reactions on 4-[ $\beta$ -chloroethyl]-<sup>307</sup> as well as 4-[3,5-dichlorotriazinyl]phenyltrimethylsilane<sup>280</sup> with amines have also been described.

As expected the dibromomethylbenzenes **63** can be hydrolyzed to give the benzaldehydes **122** (49–69%)<sup>101,169,249,250,310</sup>.



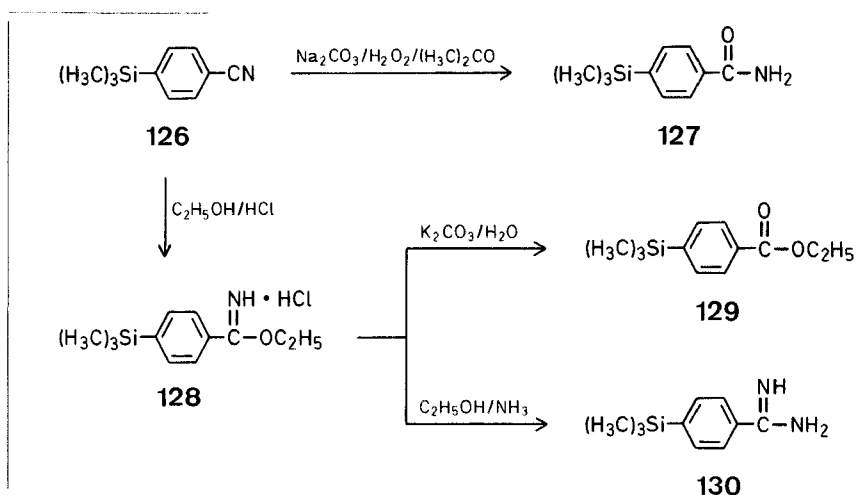
## 5.2. Functionalization of Carboxylic Acid Derivatives

Trimethylsilyl-substituted benzoic acids **123**, easily obtainable by carboxylation reactions (cf. Section 4.7.), afford the acyl chlorides **124** when treated with thionyl chloride<sup>168,272,308,311</sup>. The conversion of acyl chlorides **124** to the corresponding acyl amides **125** can be effected easily with ammonia or aniline<sup>62,144,168,308</sup>.

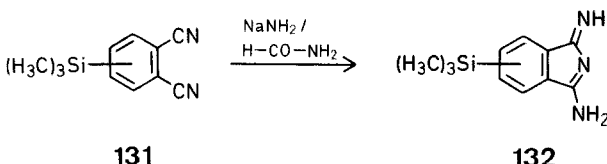


Acyl chlorides, obtained in a similar manner from 3- and 4-trimethylsilylphthalic acid, form esters on reaction with methanol<sup>312</sup> and with ammonia give acyl amides<sup>204,312</sup>.

The methyl esters of 4-trimethylsilylbenzoic acid<sup>85</sup>, 4-trimethylsilylphenylacetic acid<sup>306</sup>, and 4,4'-trimethylsilyldiphenylcarboxylic acid<sup>157</sup> can be prepared directly from the acids by using diazomethane. Another pathway to acquire derivatives of 4-trimethylsilylbenzoic acids starts from 4-cyanophenyltrimethylsilane (**126**), which according to the reaction conditions, can be converted to the amide **127** or the iminoester hydrochloride **128**. This permits the preparation of the ester **129** or the amidine **130**<sup>296</sup>.

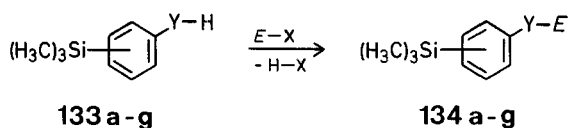


Amino-imino-isoindolenines **132** (90–92%) are obtained from phthalic dinitriles **131**<sup>204</sup>.



### 5.3. Functionalization of Hydroxy and Amino Groups

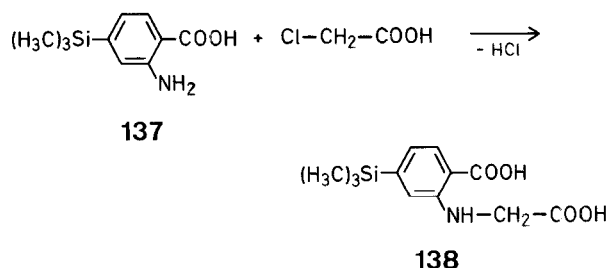
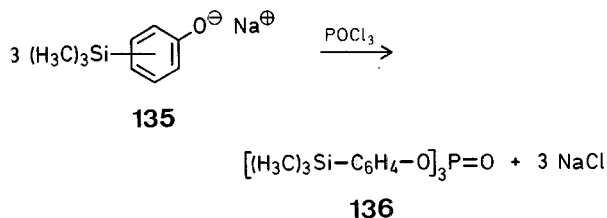
Hydroxy compounds most important in this connection are the phenols, although alcohols like 4-trimethylsilylbenzyl- or -phenylethyl alcohol can also be converted into the corresponding chloro<sup>307,309</sup> or acetyl compounds<sup>169,250</sup>, respectively. Trimethylsilylphenols and -thiophenols **133** react with various electrophiles to afford the *O*- or *S*-substituted derivatives **134**, which, in many cases, are used only to protect the functional group<sup>212,250</sup>.



|   | Y | E  | X                                | Yield [%] | Reference |
|---|---|--|----------------------------------|-----------|-----------|
| a | O | SO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> -CH <sub>3</sub> - <i>p</i> | Cl                               | 73        | 126       |
| b | O | CH <sub>3</sub>  | OSO <sub>3</sub> CH <sub>3</sub> | —         | 257       |
| c | O |  | Cl                               | 87        | 64        |
| d | S | CH <sub>3</sub>  | OSO <sub>3</sub> CH <sub>3</sub> | —         | 85        |
| e | S |  | Cl                               | 75-90     | 255       |
| f |   | H <sub>3</sub> C-CO-   | O-CO-CH <sub>3</sub>             | 90        | 257, 270  |

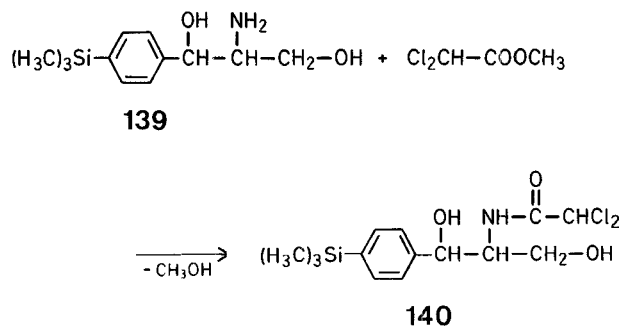
Acetylene reacts with 4-trimethylsilylthiophenol (**133g**; Y = S) to afford 4-trimethylsilylphenyl vinyl sulfide (**134g**; E = CH=CH<sub>2</sub>).

All 3 chlorine atoms of phosphoryl chloride are replaced in its reaction with trimethylsilylphenolates **135** to give **136** (64%)<sup>313</sup>.

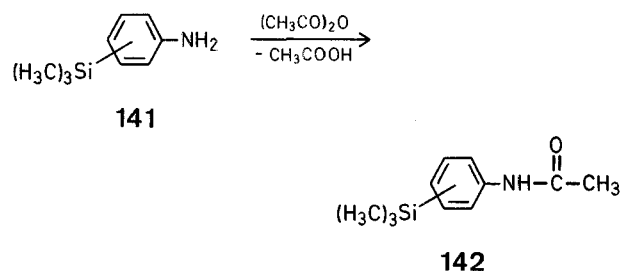


Amines undergo reactions with electrophiles analogous to the hydroxide compounds. *N*-Alkylation (44%) is found to occur in the reaction of **137** with chloroacetic acid<sup>314</sup>.

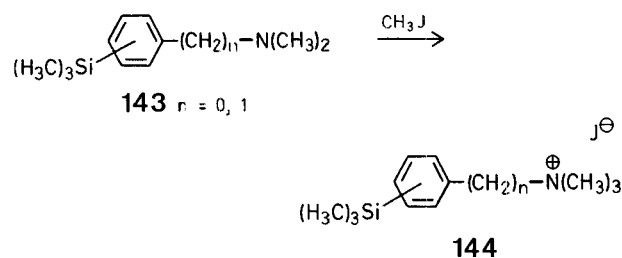
*N*-Acylation (90%) takes place exclusively in the reaction of **139** with methyl dichloroacetate<sup>307</sup>.



Anilines **141** readily react with acetic anhydride to give acetanilides **142** (90–100%)<sup>243,245,259,314</sup>.



Tertiary amines **143** can be converted to the quaternary iodides **144** without desilylation reactions<sup>278</sup> occurring simultaneously.

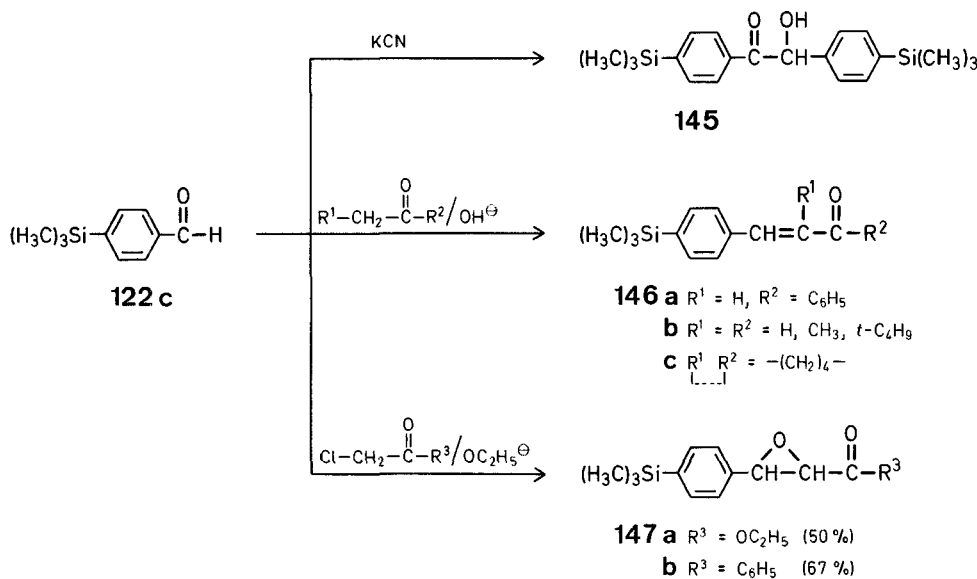


### 5.4. Condensation Reactions

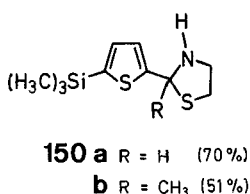
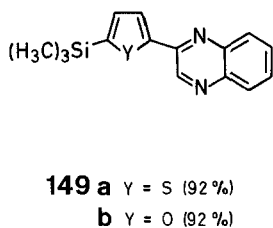
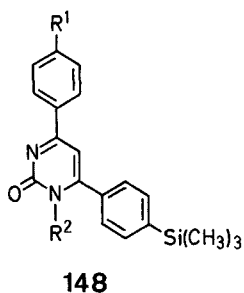
Aromatic carbonyl compounds carrying trimethylsilyl substituents undergo all types of conventional carbonyl reactions without desilylation when carried out in slightly acidic or basic medium. Since the formation of oximes, hydrazones, and semicarbazones etc., which are also used to characterize the compounds, proceeds as usual, these reactions will not be discussed here.

Benzoïn condensation<sup>296</sup>, aldol reactions<sup>296,315</sup>, and glycidic ester syntheses<sup>316</sup> employing 4-trimethylsilylbenzaldehyde (**122c**) also proceed as expected.

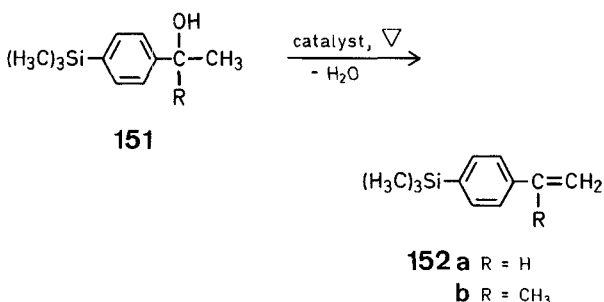
Various pyrimidines such as **148**<sup>317</sup>, quinoxalines **149**<sup>318</sup>, thiazolidines **150**<sup>319</sup>, as well as numerous tri-



methylsilyl-substituted phthalocyanin, indigoide, and triphenylmethane dyes have been prepared by condensation reactions using the appropriate trimethylsilyl carbonyl compounds<sup>204,297,314</sup>.



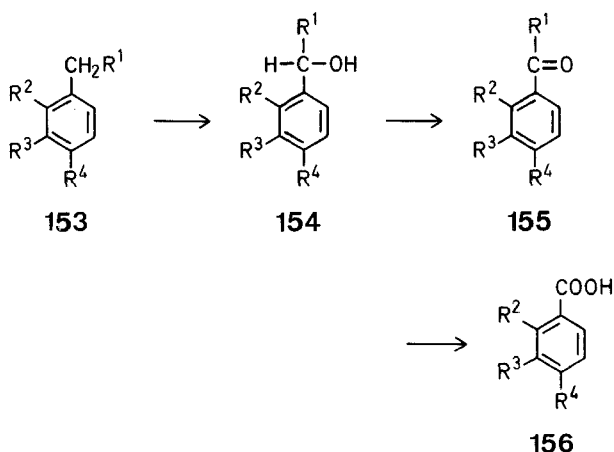
Alcohols of the type **151** in the presence of various catalysts (aluminum oxide 300–340°, 39–52%<sup>287,288</sup>; potassium hydrogen sulfate, 240°, 43%<sup>65</sup>; phosphorus pentoxide<sup>320</sup>) can be converted into styrenes **152** by thermal gas phase condensations.



Elimination of water occurs when trimethylsilylphthalic acid or trimethylsilylphenylthienylcarbinols are heated to yield the corresponding anhydride (100%)<sup>204</sup> or ethers (30%)<sup>291</sup>, respectively.

### 5.5. Oxidation Reactions

Methylbenzenes **153** ( $\text{R}^1 = \text{H}$ ), benzyl alcohols **154** ( $\text{R}^1 = \text{H}$ ), and benzaldehydes **155** ( $\text{R}^1 = \text{H}$ ) can be oxidized with increasing ease by various agents to afford the benzoic acids **156**. However, it is more difficult to stop the reaction at the carbonyl compound **155**; mixtures of acetophenones **155** ( $\text{R}^1 = \text{CH}_3$ ) and acids **156** are obtained from ethylbenzenes **153** ( $\text{R}^1 = \text{CH}_3$ ). Oppenauer oxidation of **154** ( $\text{R}^1 = \text{C}_6\text{H}_5$ ) leads to the benzophenones **155** ( $\text{R}^1 = \text{C}_6\text{H}_5$ ). Mild oxidation of the methylbenzenes **153** ( $\text{R}^1 = \text{H}$ ) in acetic anhydride gives the benzaldehydes **155** ( $\text{R}^1 = \text{H}$ ), available via the diacetate intermediate (Table 25).

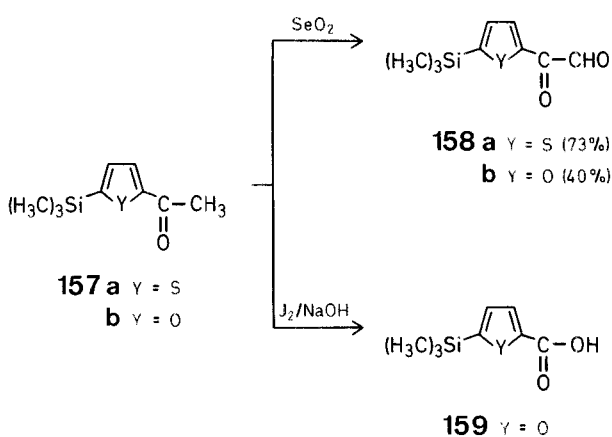


Furthermore, 4-trimethylsilylbenzaldehyde (**122c**) is obtained from the *p*-substituted benzyl bromide **62c** by employing the Sommelet<sup>308</sup> or Hass-Bender reaction (87%)<sup>250</sup>. The corresponding terephthalic, isophthalic, and phthalic acids are formed (77–92%)<sup>204,312</sup> in the oxidation of xyloltrimethylsilanes using potassium permanganate in pyridine. Acetylfurans and -thiophenes **157** are oxidized to give  $\alpha$ -

**Table 25.** Oxidation Reactions on Side Chains of Aryltrimethylsilanes

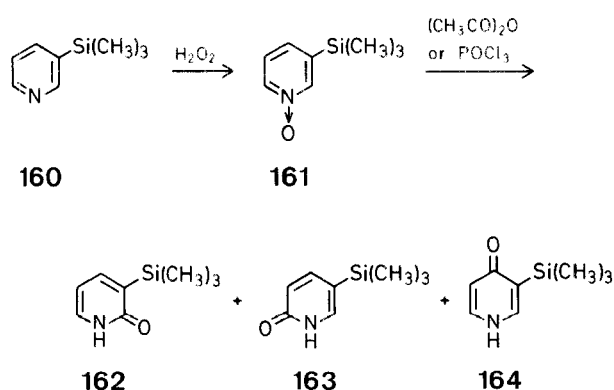
| Substrate | R <sup>1</sup>                | R <sup>2</sup>                     | R <sup>3</sup>                     | R <sup>4</sup>                     | Oxidising agent   | Product   | Yield [%] | Reference |
|-----------|-------------------------------|------------------------------------|------------------------------------|------------------------------------|---|-----------|-----------|-----------|
| 153       | H                             | (H <sub>3</sub> C) <sub>3</sub> Si | H                                  | H                                  | KMnO <sub>4</sub>   | 156       | 21        | 168       |
| 153       | H                             | H                                  | H                                  | (H <sub>3</sub> C) <sub>3</sub> Si | KMnO <sub>4</sub>   | 156       | 74        | 85, 308   |
| 154       | H                             | H                                  | H                                  | (H <sub>3</sub> C) <sub>3</sub> Si | KMnO <sub>4</sub>   | 156       | —         | 310       |
| 155       | H                             | H                                  | (H <sub>3</sub> C) <sub>3</sub> Si | H                                  | O <sub>2</sub>  | 156       | 100       | 310       |
| 155       | H                             | H                                  | H                                  | (H <sub>3</sub> C) <sub>3</sub> Si | O <sub>2</sub>  | 156       | 100       | 310       |
| 153       | H                             | H <sub>3</sub> C CO NH             | H                                  | (H <sub>3</sub> C) <sub>3</sub> Si | KMnO <sub>4</sub>   | 156       | 85        | 310       |
| 153       | H <sub>3</sub> C              | H                                  | (H <sub>3</sub> C) <sub>3</sub> Si | H                                  | CaCO <sub>3</sub> /O <sub>2</sub>                           | 155 + 156 | 15 + 11   | 133, 249  |
| 153       | H <sub>3</sub> C              | (H <sub>3</sub> C) <sub>3</sub> Si | H                                  | H                                  | CaCO <sub>3</sub> /O <sub>2</sub>                           | 155 + 156 | 11 + 12   | 133, 249  |
| 153       | H <sub>3</sub> C              | H                                  | H                                  | (H <sub>3</sub> C) <sub>3</sub> Si | CaCO <sub>3</sub> /O <sub>2</sub>                           | 155 + 156 | 20 + 8    | 249       |
| 153       | H                             | O <sub>2</sub> N                   | H                                  | (H <sub>3</sub> C) <sub>3</sub> Si | CrO <sub>3</sub> /Ac <sub>2</sub> O                         | 155       | 19        | 314       |
| 154       | C <sub>6</sub> H <sub>5</sub> | H                                  | H                                  | (H <sub>3</sub> C) <sub>3</sub> Si | Al(OC <sub>4</sub> H <sub>9</sub> - <i>t</i> ) <sub>3</sub> | 155       | 23        | 295       |

keto aldehydes **158** by using selenium oxide<sup>318</sup> or to carboxylic acids **159** by using sodium hypiodide<sup>293</sup>.



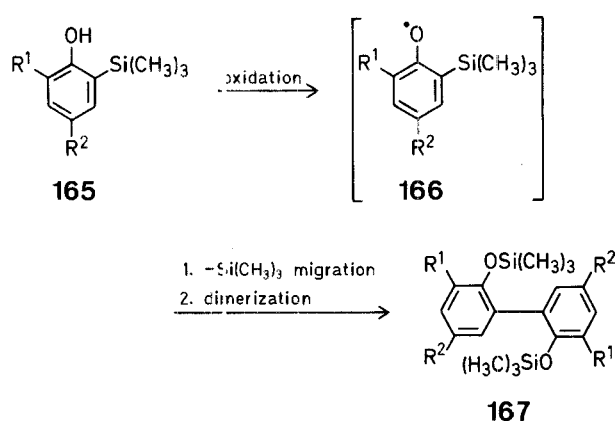
The epoxidation of 4-trimethylsilylstyrene using perbenzoic acid (50%)<sup>65</sup>, the oxidation of 2-, 3-, and 4-trimethylsilyldibenzothiophene<sup>141,153</sup> using hydrogen peroxide to give the corresponding sulfones (42–98%), and the oxidation of 2- or 3-trimethylsilyl-4-amino-phenol<sup>321</sup> with potassium dichromate/sulfuric acid to yield the corresponding *p*-benzoquinones are further oxidation reactions involving functional groups of aryl- and heteroaryltrimethylsilanes. The oxidation of 3-nitroso-4-trimethylsilylpyrazole leads to the nitro compound<sup>261</sup>.

The oxidative introduction of oxygen functions into the nucleus has been applied in the preparation of



the pyridones **162–164** from 3-pyridyltrimethylsilane (**160**)<sup>154</sup> and of 2-trimethylsilyl-*p*-benzoquinone from 4-aminophenols using potassium dichromate/sulfuric acid<sup>322</sup>.

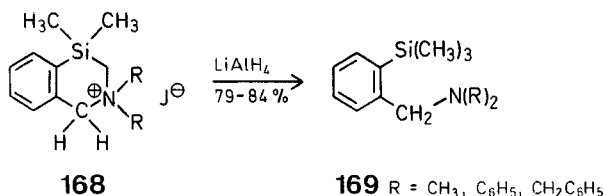
Razuvaev et al.<sup>98,214,323</sup> have exhaustively investigated the one-electron oxidation of sterically hindered silicon-containing phenols **165** [R<sup>1</sup>, R<sup>2</sup> = CH<sub>3</sub>, *i*-C<sub>3</sub>H<sub>7</sub>, *t*-C<sub>4</sub>H<sub>9</sub>, Si(CH<sub>3</sub>)<sub>3</sub>, etc.] with various agents [e.g. lead oxide, potassium hexacyanoferrate(III), copper/pyridine/oxygen, *t*-butyl ether, phenylmercury(II) hydroxide, etc.). The reaction goes through the intermediate free phenoxy radicals **166** which rearrange by migration of the trimethylsilyl group and undergo subsequent dimerization to afford the 2,2'-bis[trimethylsiloxy]biphenyls **167**. Trimethylsilyl-substituted quinones are found as by-products.



## 5.6. Reduction Reactions

Metal hydrides, such as lithium aluminum hydride, sodium borohydride etc. do not affect the carbon-silicon bonds in aryltrimethylsilanes. They therefore provide a convenient method for reduction of various functional groups. Using sodium borohydride the conversion of trimethylsilylacetophenones into the alcohols<sup>65</sup> is possible under mild conditions as well as the hydrogenolytic cleavage of trimethylsilylthienyl-thiazolidines (68–71%)<sup>319</sup>. Employing the more reactive lithium aluminum hydride, trimethyl-

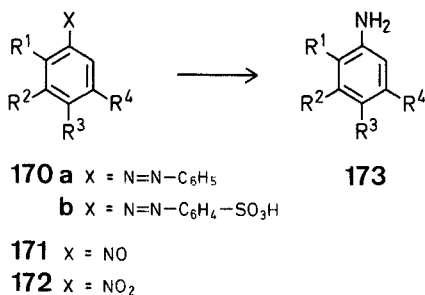
silylaryl derivatives of carboxylic acids and serine can be reduced to yield the corresponding alcohols (up to 90%)<sup>307</sup>. Corresponding nitriles are reduced to primary amines<sup>296,307</sup>. *N*-Substituted amines of the type **169** are obtained by reduction of acyl amides<sup>163</sup> or by reductive cleavage of **168** using lithium aluminum hydride<sup>324</sup>.



Reduction of trimethylsilyl-substituted phosphine oxides by lithium aluminum hydride gives the phosphines<sup>277</sup>.

Other procedures for the convenient preparation of benzyl alcohols from benzaldehydes are, for example, the treatment with tin(II) chloride/hydrogen chloride<sup>296</sup>, normal or crossed (formaldehyde/OH<sup>-</sup>) Cannizzaro reactions<sup>296,325</sup> and the reduction by trialkylsilanes in the presence of zinc chloride<sup>326</sup>.

Reduction processes are the most important methods for the preparation of aromatic amines. This also applies to the trimethylsilyl derivatives. Thus, azo compounds **170**, nitroso- **171**, or nitroaromatic compounds **172** can be converted into the amines **173** if the appropriate reducing agents are applied (Table 26).



### 5.7. Metal Complexes of Aryl- and Heteroaryltrimethylsilanes

By the complexation of the  $\pi$ -system of aryl- or of the nitrogen atom of heteroaryltrimethylsilanes, the reactivity of the carbon-silicon bond can be drastically altered.

Metallation of ( $\eta$ -benzene)-( $\eta$ -pentafluorobenzene)chromium with *n*-butyllithium and bis[benzene]chromium with *n*-butyllithium/tetramethylethylenediamine and subsequent silylation affords  $\{(\text{C}_6\text{H}_6)_2\text{Cr}[\text{C}_6\text{H}_5-\text{Si}(\text{CH}_3)_3]\}$  (78%)<sup>327</sup> and  $[\text{C}_6\text{H}_5-\text{Si}(\text{CH}_3)_3]_2\text{Cr}$  (37%)<sup>32</sup>, respectively. Furthermore, oxidation of the chromium atoms in these complexes can also be used to cause a strong variation in the reactivity of the carbon-silicon bond<sup>328</sup>. The chromium tricarbonyl complexes of phenyltrimethylsilane and the bis[trimethylsilyl]benzenes **64a-c** are formed when these compounds are heated together with hexacarbonylchromium<sup>329,330</sup>.

#### Trimethylsilylbenzene Chromium Tricarbonyl<sup>329</sup>:

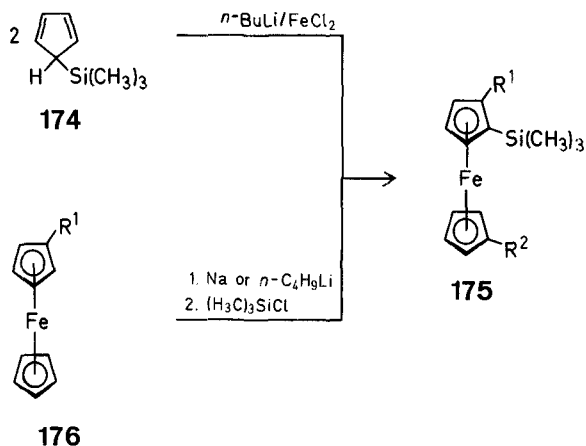
A mixture of hexacarbonylchromium (2.2 g, 10 mmol) and phenyltrimethylsilane (10 ml) is maintained at 170–175° for 36 h under an argon atmosphere in a flask equipped with an air condenser topped with a water-cooled condenser. During this time the hexacarbonylchromium which sublimes into the air condenser is periodically pushed back into the reaction flask with a long spatula. A yellow colour develops slowly in the reaction mixture, and a small amount of solid is formed. The mixture is then cooled and diluted with ether (100 ml). Filtration through a short column of deactivated alumina is followed by removal of volatiles at reduced pressure. The yellow crystalline residue is recrystallized from aqueous ethanol to give the product; yield: 0.56 g (20%); m.p. 72–73°. An analytical sample was sublimed at 60–65°/0.01 torr.

Ferrocenyltrimethylsilanes **175** [R<sup>1</sup> = H, R<sup>2</sup> = Si(CH<sub>3</sub>)<sub>3</sub>; 50%]<sup>331</sup> are prepared from cyclopentadienyltrimethylsilanes **174** using *n*-butyllithium and iron(II) chloride. Metallation of ferrocenes **176** (R<sup>1</sup> = H) with sodium<sup>332</sup> or *n*-butyllithium<sup>333,334</sup> and subsequent silylation affords mixtures of **175** (R<sup>1</sup> = R<sup>2</sup> = H; 19–23%) and **175** [R<sup>1</sup> = H, R<sup>2</sup> = Si(CH<sub>3</sub>)<sub>3</sub>; 27–50%]; in the case of (dimethylami-

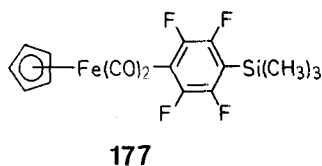
**Table 26.** Trimethylsilyl-Substituted Aminobenzenes **173** via Reduction of Azo, Nitroso, or Nitro Compounds

| Type        | R <sup>1</sup>                     | R <sup>2</sup>                     | R <sup>3</sup>                     | R <sup>4</sup>                     | Reducing Agent                                | Yield [%] | Reference |
|-------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|---|-----------|-----------|
| <b>170a</b> | H                                  | (H <sub>3</sub> C) <sub>3</sub> Si | OH                                 | H                                  | Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> | —         | 258       |
| <b>170b</b> | (H <sub>3</sub> C) <sub>3</sub> Si | H                                  | OH                                 | H                                  | Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> | 95        | 257       |
| <b>171</b>  | (H <sub>3</sub> C) <sub>3</sub> Si | H                                  | H                                  | OH                                 | Pd/C, H <sub>2</sub>                          | —         | 257       |
| <b>171</b>  | (H <sub>3</sub> C) <sub>3</sub> Si | H                                  | N(CH <sub>3</sub> ) <sub>2</sub>   | H                                  | Pd/C, H <sub>2</sub>                          | —         | 245       |
| <b>172</b>  | (H <sub>3</sub> C) <sub>3</sub> Si | H                                  | H                                  | H                                  | Raney-Ni/H <sub>2</sub>                       | 83        | 144       |
| <b>172</b>  | H                                  | (H <sub>3</sub> C) <sub>3</sub> Si | H                                  | H                                  | Raney-Ni/H <sub>2</sub>                       | 85        | 79, 144   |
| <b>172</b>  | H                                  | H                                  | (H <sub>3</sub> C) <sub>3</sub> Si | H                                  | Pd/C, H <sub>2</sub>                          | —         | 243, 265  |
| <b>172</b>  | H                                  | H                                  | (H <sub>3</sub> C) <sub>3</sub> Si | H                                  | Raney-Ni/H <sub>2</sub>                       | 75        | 79, 144   |
| <b>172</b>  | (H <sub>3</sub> C) <sub>3</sub> Si | H                                  | Cl                                 | H                                  | Pd/C, H <sub>2</sub>                          | —         | 243       |
| <b>172</b>  | (H <sub>3</sub> C) <sub>3</sub> Si | H                                  | (H <sub>3</sub> C) <sub>3</sub> Si | H                                  | Raney-Ni/H <sub>2</sub>                       | 75        | 271       |
| <b>172</b>  | NHCOCH <sub>3</sub>                | H                                  | (H <sub>3</sub> C) <sub>3</sub> Si | H                                  | Pd/C, H <sub>2</sub>                          | —         | 243       |
| <b>172</b>  | (H <sub>3</sub> C) <sub>3</sub> Si | H                                  | (H <sub>3</sub> C) <sub>2</sub> N  | H                                  | Pd/C, H <sub>2</sub>                          | 86        | 245       |
| <b>172</b>  | CH <sub>3</sub>                    | H                                  | H                                  | (H <sub>3</sub> C) <sub>3</sub> Si | Raney-Ni/H <sub>2</sub>                       | 90        | 314       |

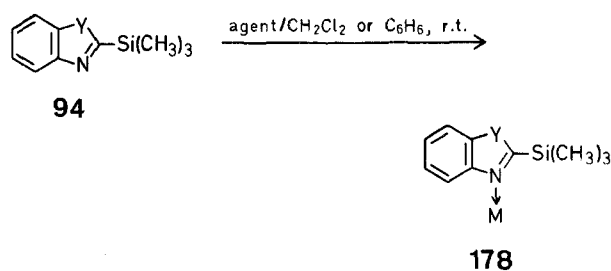
no)-methylferrocene **176** [ $R^1 = \text{CH}_2\text{N}(\text{CH}_3)_2$ ] "ortho-metallation" favours selective reaction to give **175** [ $R^1 = \text{CH}_2\text{N}(\text{CH}_3)_2$ ,  $R^2 = \text{H}$ ; 79%]<sup>335</sup>.



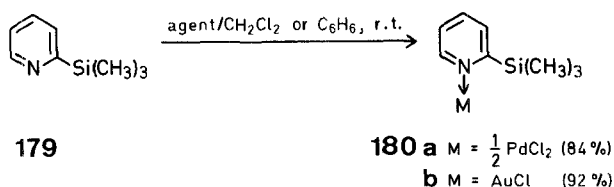
The methiodide of **175** [ $R^1 = \text{CH}_2\text{N}(\text{CH}_3)_2$ ,  $R^2 = \text{H}$ ] readily undergoes nucleophilic substitution of the trimethylamino group by aqueous hydroxide (85%), phenoxide (85%), aniline (95%), and piperidine (66%)<sup>335</sup>. The reaction of the  $\pi$ -cyclopentadienyl-iron dicarbonyl anion with pentafluorophenyltrimethylsilane gives **177**<sup>336</sup>.



The palladium(II)<sup>337</sup> and gold(I)<sup>338</sup> complexes **178** and **180** of the silanes **94** and **179** are formed, when



| Agent  | Y                | M                           | Yield [%] | Reference |
|--|------------------|-----------------------------|-----------|-----------|
| $\text{PdCl}_2(\text{C}_6\text{H}_5\text{CN})_2$ | S                | $\frac{1}{2} \text{PdCl}_2$ | 91        | 337       |
| $\text{PdCl}_2(\text{C}_6\text{H}_5\text{CN})_2$ | NH               | $\frac{1}{2} \text{PdCl}_2$ | 63        | 337       |
| $\text{Au}(\text{CO})\text{Cl}$                  | S                | AuCl                        | 73        | 338       |
| $\text{C}_7\text{H}_5\text{NS} \text{ GeCl}_2$   | NCH <sub>3</sub> | $\text{GeCl}_2$             | 60        | 304       |

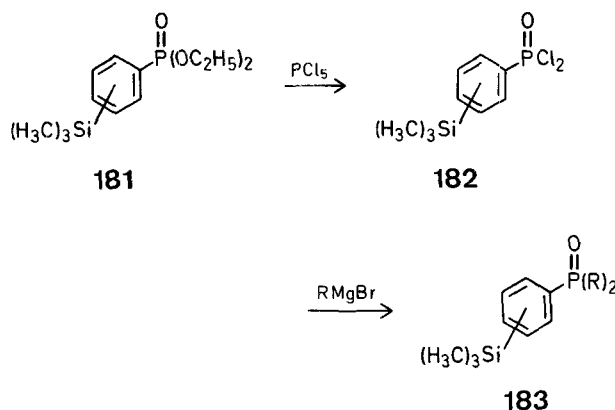


these compounds react with  $\text{PdCl}_2(\text{C}_6\text{H}_5\text{CN})_2$ , gold chloride or gold carbonyl chloride. Dichlorogermylene complexes **178** are obtained in a similar way<sup>304</sup>. The carbon-silicon bond of all complexes proves to be less reactive than that of the free silanes.

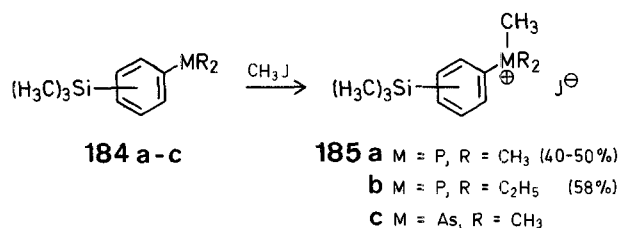
### 5.8. Miscellaneous

In closing, some types of reactions and compounds that do not readily fit into one of above categories should be mentioned.

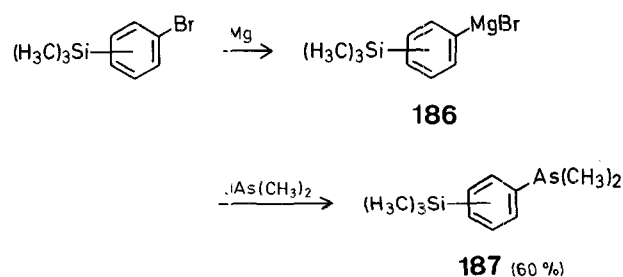
The phosphonic esters **181** react with phosphorus pentachloride to yield the dichlorides **182** which can be converted into the phosphine oxides **183** using Grignard agents or into the phosphonic acids, when hydrolyzed<sup>277,339</sup>.



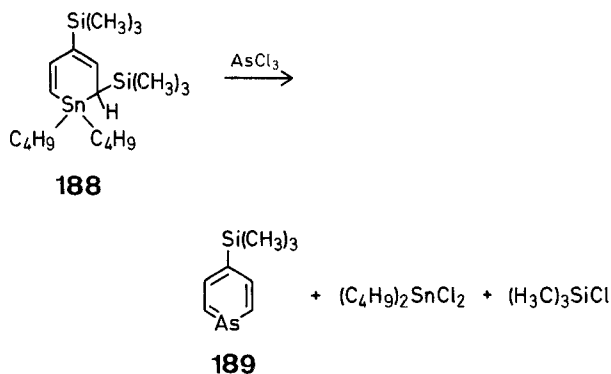
Halogenation and saponification are similarly applicable to the trimethylsilylphenylmethanephosphonates<sup>277</sup>. Similar to the tertiary amines **143** (cf. Section 5.3.), the phosphines and arsines **184** can be converted into the corresponding quaternary iodides **185**<sup>277,278,339</sup>.



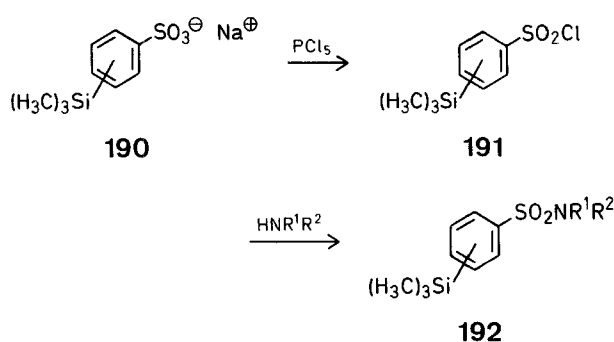
Dimethylarsino groups are introduced into aromatic rings like most of the phosphorus substituents (cf. Section 4.4.). The organometallic compounds **186**<sup>278</sup> are involved as intermediates.



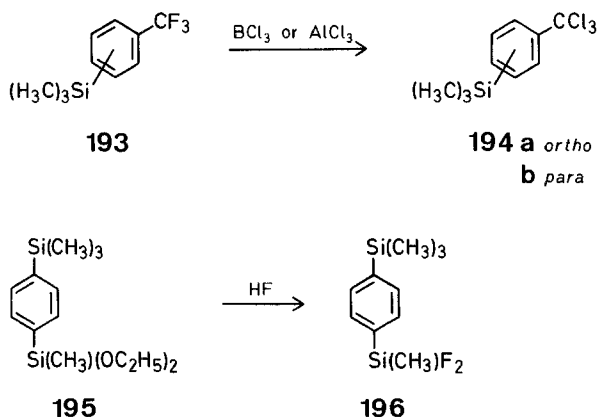
4-Trimethylsilyl-1-arsabenzene (**189**) can be prepared in 83% yield by treating **188** with arsenic(III) chloride<sup>340</sup>.



Sulfonyl chlorides **191** are prepared from salts of sulfonic acids **190** employing phosphorus pentachloride<sup>252</sup>, thus enabling the preparation of sulfonamides **192**<sup>252, 309</sup>.



Reactions involving halide exchange on trifluoromethylbenzenes **193**<sup>51, 341</sup> to give **194** and on ethoxysilanes **195**<sup>252</sup> to yield **196** have been carried out.



## 6. Conclusions

Although the number of publications concerning aryl- or heteroaryltrimethylsilanes is increasing markedly, it does not seem very likely that dramatically different preparative methods from those described here can be expected for this class of compounds.

In contrast, the better understanding of their reactions and, therefore, of the scope of their preparative utility is still in its infancy and, thus, the system holds promise for interesting future developments similar to that of the chemistry of vinylsilanes and silyl enol ethers. It is hoped that this article has provided some stimulation for achieving that development.

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