

## Reactivity of Nitro- and Nitroso-arenes with Vinyl Grignard Reagents: Synthesis of 2-(Trimethylsilyl)indoles

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The reaction of nitrosoarenes and 1-(trimethylsilyl)vinylmagnesium bromide in dibutyl ether represents a useful tool for the synthesis of 2-(trimethylsilyl)indoles by cyclisation of benzene derivatives. The use of more common ethers as the solvent leads to large amounts of azo and azoxy derivatives. Conversely, the reaction of nitroarenes and 1-(trimethylsilyl)vinylmagnesium bromide gives conjugate addition products. The reasons for this behaviour are discussed.

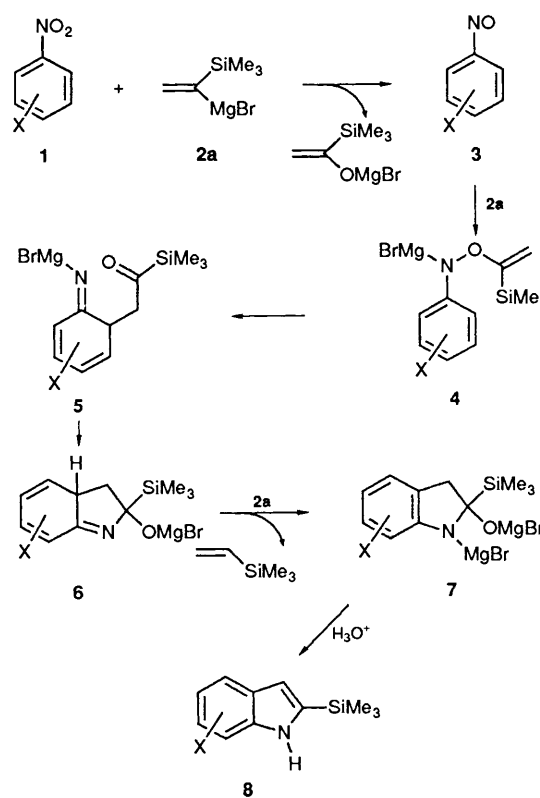
Indol-2-yl ketones have been widely employed as key intermediates in the synthesis of indole alkaloids. Unfortunately, neither electrophilic nor nucleophilic substitutions, which both occur at the 3-position<sup>1</sup> of the indole ring, can offer a straightforward route to their preparation. In recent years, strategies directed to substitution at the 2-position<sup>1</sup> have been developed. For example, 2-lithioindoles derived from a variety of *N*-protected indoles have been routinely used to functionalise this position.<sup>2</sup>

Masked indol-2-yl ketones have been prepared by reaction of 2-lithioindoles with chlorodithiane.<sup>3</sup> On the other hand, an intriguing route to indol-2-yl ketones is to perform a Friedel-Crafts alkylation on 2-(trimethylsilyl)indoles,<sup>4</sup> utilising the well known *ipso*-directing ability of silicon towards electrophilic substitutions. However, the synthesis of these derivatives requires an extant indole nucleus,<sup>5</sup> whose functionalisation at the normally unreactive benzene ring is problematic. The only general method for this purpose involves halogen-metal exchange of bromoindoles,<sup>6</sup> which must be synthesized by a *de novo* ring construction. Preparation of 2-(trimethylsilyl)indoles by direct cyclisation is an until now undeveloped strategy despite the inherent directness of such an approach. The only available method<sup>7</sup> is based on cyclisation of alkynylanilines promoted by sodium tetraurate as the catalyst. However, this reaction affords indoles in low yield, starting from difficultly available reagents and using a very expensive catalyst.

Some of our own work<sup>8</sup> on the reactivity of Grignard reagents with nitro- and nitroso-arenes recently provided a useful method for the synthesis of indoles.<sup>9</sup> We found that nitrosoarenes **3** react with 2 mol equiv. of vinylmagnesium halide **2** via 1,2-addition to give an *N*-aryl-*O*-vinylhydroxylamino magnesium salt **4**, which undergoes sigmatropic rearrangement, ring closure, and finally re-aromatisation to afford indoles **8** (Scheme 1). Moreover, the reaction of nitroarenes **1** requires a three-fold excess of Grignard reagent, since the first stage of the reaction is the reduction to nitrosoarene by 1 mol equiv. of organomagnesium halide. This reaction appeared to be a new and useful route to the synthesis of 2-(trimethylsilyl)indoles when starting from 1-(trimethylsilyl)vinylmagnesium bromide<sup>10</sup> as the alkylating agent.

### Results and Discussion

**Reaction of Nitrosoarenes.**—When a two-fold excess of 1-(trimethylsilyl)vinylmagnesium bromide was allowed to react with 2-nitrosotoluene in dibutyl ether at  $-50^{\circ}\text{C}$  and the mixture was then allowed to warm at  $0^{\circ}\text{C}$  overnight, 7-methyl-2-(trimethylsilyl)indole **8aa** was recovered in 48% yield (Table



Scheme 1

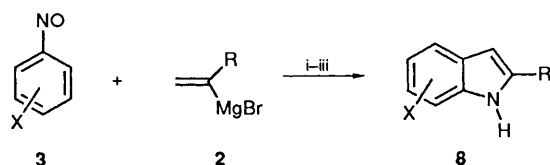
1). The reaction shows a general character and can be applied to a large series of substituted nitrosoarenes to give indoles bearing different substituents. *para*-Substituted nitrosobenzenes afforded 5-substituted 2-(trimethylsilyl)indoles in better yield than when they reacted with unsubstituted vinyl Grignard reagent.<sup>9</sup> *meta*-Substituted nitrosobenzenes afforded both 4- and 6-substituted 2-(trimethylsilyl)indoles in a *ca.* 1:1 ratio (Scheme 2).

It should be noted that indole yields are comparable with those reported in the cyclisation of alkynylanilines, but the present method starts from more available materials and does not employ expensive catalysts. Therefore it represents a valuable alternative to the synthesis of 2-(trimethylsilyl)indoles by a *de novo* ring construction route.

The use of dibutyl ether is essential for the reaction. Use of the more common tetrahydrofuran (THF) or diethyl ether provides large amounts of azo and azoxy derivatives (Table 2).

**Table 1** Reaction of 1-(trimethylsilyl)vinylmagnesium bromide and nitrosoarenes in dibutyl ether at  $-50^{\circ}\text{C}$ , then overnight at  $0^{\circ}\text{C}$ 

Nitrosoarene	Grignard reagent	Indole product	Yield (%)
3a	2a	8aa	48
3a	2b	8ab	46
3b	2a	8ba	11
		8b'a	12
3c	2a	8ca	23
3d	2a	8da	35
3e	2a	8ea	50
3f	2a	8fa	18
		8f'a	14
3g	2a	8ga	35
3h	2a	8ha	42
3i	2a	8ia	39
3j	2a	8ja	42
3k	2a	8ka	28



3 a; X = 2-Me, b; X = 3-Me, c; X = 4-Me, d; X = H, e; X = 2-Cl, f; X = 3-Cl, g; X = 4-Cl, h; X = 2-Br, i; X = 2-Et, j; X = 2,4-Cl, k, X = 2-Me-4-PhO. 2 a; R = SiMe<sub>3</sub>, b; R = Ph. 8 aa; R = SiMe<sub>3</sub>, X = 7-Me, ab; R = Ph, X = 7-Me, ba; R = SiMe<sub>3</sub>, X = 4-Me, b'a; R = SiMe<sub>3</sub>, X = 6-Me, ca; R = SiMe<sub>3</sub>, X = 5-Me, da; R = SiMe<sub>3</sub>, X = H, ea; R = SiMe<sub>3</sub>, X = 7-Cl, fa; R = SiMe<sub>3</sub>, X = 4-Cl, f'a; R = SiMe<sub>3</sub>, X = 6-Cl, ga; R = SiMe<sub>3</sub>, X = 5-Cl, ha; R = SiMe<sub>3</sub>, X = 7-Br, ia; R = SiMe<sub>3</sub>, X = 7-Et, ja; R = SiMe<sub>3</sub>, X = 5,7-Cl, ka; R = SiMe<sub>2</sub>, X = 7-Me-5-PhO

**Scheme 2** Reagents and conditions: i, Bu<sub>2</sub>O,  $-50^{\circ}\text{C}$ ; ii,  $0^{\circ}\text{C}$ , overnight; iii, aq. NH<sub>4</sub>Cl

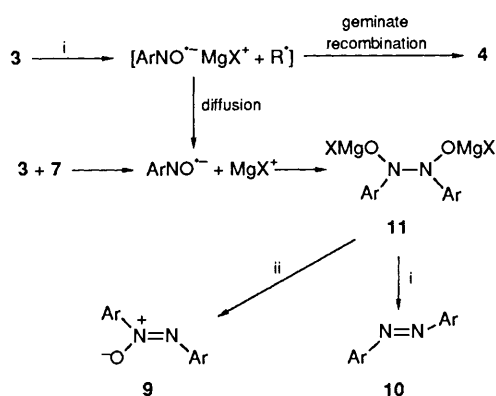
**Table 2** Reaction of *o*-nitrosotoluene and 1-(trimethylsilyl)vinylmagnesium bromide (2 mol equiv.) under different reaction conditions

Solvent	Conditions	Yield (%)		
		8aa	9a	10a
THF	$0^{\circ}\text{C}$ , 10 min	12	31	17
THF <sup>a</sup>	$0^{\circ}\text{C}$ , 10 min		70	27
THF	$-50^{\circ}\text{C}$ , 10 min; overnight, $0^{\circ}\text{C}$	14		45
Et <sub>2</sub> O	$-50^{\circ}\text{C}$ , 10 min; overnight, $0^{\circ}\text{C}$	20		
Bu <sub>2</sub> O	$-50^{\circ}\text{C}$ , 10 min; 30 min, $0^{\circ}\text{C}$	30		
Bu <sub>2</sub> O	$-50^{\circ}\text{C}$ , 10 min; overnight, $0^{\circ}\text{C}$	48		
Bu <sub>2</sub> O	$-50^{\circ}\text{C}$ , 10 min; 48 h, $0^{\circ}\text{C}$	42		
Bu <sup>t</sup> Ph	$-50^{\circ}\text{C}$ , 10 min; overnight, $0^{\circ}\text{C}$	36		

<sup>a</sup> 1-(Trimethylsilyl)vinylolithium is employed.

It is well known that azoxy derivatives can arise from coupling of two nitrosoarenes radical anions,<sup>11</sup> and azobenzenes from reduction of the former compounds by an excess of Grignard reagent.<sup>9</sup> Nitrosoarene radical anions can be generated by electron transfer from intermediates 4 or 7 to nitrosoarene 3. This pathway can be depressed by lowering the nitrosoarene concentration and by increasing that of the Grignard reagent as previously described.<sup>9</sup> Nevertheless, even by dropwise addition of nitrosoarene to the Grignard reagent solution, high amounts of azo and azoxy derivatives are obtained (Table 2).

We have previously demonstrated that the first interaction between nitroarenes and Grignard reagents is an electron transfer which gives nitrosoarene radical anions and alkyl radicals.<sup>12</sup> Since nitrosoarenes are better electron-accepting

**Scheme 3** Reagents: i, RMgX; ii, aq. NH<sub>4</sub>Cl

substrates than are nitro derivatives, a further source of azoxy derivatives can be the coupling of nitrosoarene radical anions which escape the 'in cage' recombination with their geminate partner (*i.e.*, the trimethylsilylvinyl radicals) (Scheme 3). Therefore the maximum yield of addition product must be obtained when a weakly polar solvent such as dibutyl ether is employed. On the other hand, a more polar solvent such as THF and the use of 1-(trimethylsilyl)vinylolithium instead of the magnesium derivative must favour redox products since it may be expected that neutral radicals collapse more easily upon reaction with a radical anion when the other has less anionic character.<sup>12</sup> In fact, the reaction of 1-(trimethylsilyl)vinylolithium with 2-nitrosotoluene in THF gives quantitative formation of azoxytoluene.

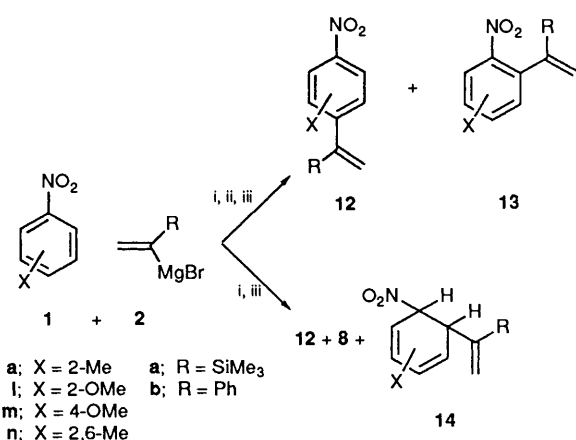
**Reaction of Nitroarenes.**—The ready availability of nitroarenes and the results of the reactivity of vinylmagnesium bromide<sup>9</sup> with these substrates prompted us to perform the reaction of 2-nitrotoluene and 1-(trimethylsilyl)vinylmagnesium bromide notwithstanding the necessity of a large excess of the more expensive reactant. Unfortunately, when 3 mol equiv. of 1-(trimethylsilyl)vinylmagnesium bromide were allowed to react with 1 mol equiv. of 2-nitrotoluene in THF at  $0^{\circ}\text{C}$ , followed by quenching with aq. ammonium chloride, only a 12% yield of 7-methyl-2-(trimethylsilyl)indole 8aa together with 2-methyl-4-(1-trimethylsilylvinyl)nitrobenzene 12aa and another uncharacterised product were recovered.

The same reaction mixture oxidized with DDQ\* in THF at  $0^{\circ}\text{C}$  for 2 h gave an 11% yield of 2-methyl-4-(1-trimethylsilylvinyl)nitrobenzene 12aa and 2-methyl-6-(1-trimethylsilylvinyl)nitrobenzene† 13aa (Scheme 4). The latter product is very likely to be the oxidised form of the uncharacterised product of the reaction quenched with NH<sub>4</sub>Cl. We previously found<sup>13</sup> that 1,6-addition products are more easily oxidised by air than are 1,4-addition products.

These findings can be arranged in a single-electron-transfer pathway by considering that the bulk and the geometry of the radical anion can influence the direction of attack. If strong steric hindrance is exerted by the substituent *ortho* to the nitro group the 1-(trimethylsilyl)vinyl radical cannot bind to the oxygen atoms and therefore it prefers the less hindered ring position. 2-Nitro-*m*-xylene 1n gives 2,6-dimethyl-4-(1-trimethylsilylvinyl)nitrobenzene 12na in 61% yield. This trend is a constant finding in the reaction of Grignard reagents and nitroarenes, when 1,2-addition is preferred to conjugate

\* 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone.

† Indole was neither recovered from this reaction nor observed by GC-MS analysis. It is likely that a reaction between the oxidant and the precursor of the indole occurs and that the product is not isolable.



**Scheme 4** Reagents and conditions: i, THF, 0 °C, 10 min; ii, DDQ, 0 °C, 2 h; iii, aq. NH<sub>4</sub>Cl

**Table 3** Reaction of 1-(trimethylsilyl)-**2a** or 1-phenyl-vinylmagnesium bromide **2b** and nitroarenes in THF at 0 °C, followed by oxidation with DDQ

Nitroarene	Grignard reagent	Yield (%)		Notes
		<b>12</b>	<b>13</b>	
<b>1a</b>	<b>2a</b>	11	10	<i>a</i>
<b>1a</b>	<b>2b</b>	27	13	
<b>1l</b>	<b>2a</b>	20	7	
<b>1m</b>	<b>2a</b>		37	<i>b, c</i>
<b>1n</b>	<b>2a</b>	61		
<b>1o</b>	<b>2a</b>	54		<i>d</i>

<sup>a</sup> The reaction mixture was quenched with aq. NH<sub>4</sub>Cl without oxidation and gave **8aa** (12%) together with **12aa** (9%) and another, uncharacterised product. <sup>b</sup> The reaction of **1m** carried out in 1,2-dimethoxyethane as solvent gave **13ma** in 20% yield. The reaction carried out in THF at -70 °C, followed by oxidation with DDQ at 0 °C for 2 h, gave **13ma** in 15% yield. The reaction of **1m** carried out in THF at reflux, followed by oxidation with DDQ at the same temperature for 1 h, gave **13ma** in 25% yield. <sup>c</sup> The reaction mixture was quenched with aq. NH<sub>4</sub>Cl without oxidation and gave **8ma** (18%) together with another, uncharacterised product. <sup>d</sup> **1o**: 2-Methoxy-1-nitronaphthalene; **12oa**: 2-methoxy-1-nitro-4-[1-(trimethylsilyl)vinyl]naphthalene.

addition. It was found<sup>14</sup> that, in the reaction of allyl Grignard reagents and nitroarenes, an increase in steric hindrance in both the nitroarene and the Grignard reagent enhances ring alkylation to the detriment of attack at the nitro group. Moreover,  $\alpha$ -styryl radicals are known to assume a planar geometry with the unpaired electron in a p-orbital.<sup>15</sup> The bulk of a trimethylsilyl group may force the 1-(trimethylsilyl)vinyl radical to adopt this geometry too. The reaction of  $\alpha$ -styrylmagnesium bromide with 2-nitrotoluene provides ring-alkylated products rather than the corresponding 2-phenylindole. On the other hand, by carrying out the reaction of  $\alpha$ -styrylmagnesium bromide with 2-nitrosotoluene under the conditions described above, 7-methyl-2-phenylindole **8ab** was recovered in 46% yield.

It should be noted that the reaction of nitroarenes and 1-(trimethylsilyl)vinylmagnesium bromide allows the formation of nitrostyrenes, which cannot be obtained with less sophisticated reagents.<sup>9</sup> When the *ortho* positions are substituted this synthesis gives comparable yields with those of other, previously known preparations.<sup>16</sup>

In conclusion, the reaction of 1-(trimethylsilyl)vinylmagnesium bromide with nitro- and nitroso-arenes provides a valuable entry both to 2-(trimethylsilyl)indoles and to [1-(trimethylsilyl)vinyl]nitrobenzenes depending on the reactants

employed. There remains, however, an unanswered question: how can the efficiency of the indole reaction be increased and the formation of polymeric material be avoided? This topic is currently being investigated in our laboratory.

## Experimental

<sup>1</sup>H NMR spectra were recorded with a Varian EM360L instrument. Chemical shifts are given in ppm from Me<sub>4</sub>Si as external standard in CDCl<sub>3</sub> solutions. Coupling constants (*J*) are given in Hz. IR spectra were recorded with a Perkin-Elmer FT 1600 spectrometer. Mass spectra were recorded with a VG 7070 spectrometer or with an HP 59970 workstation formed by an HP-5890 gas chromatograph equipped with a methylsilicone capillary column and an HP-5970 mass detector. M.p.s are uncorrected and were determined with a Buchi apparatus. THF and diethyl ether were dried by reflux over sodium wire until the blue colour of sodium benzophenone ketyl persisted, and then distillation into a dry receiver under nitrogen. *tert*-Butylbenzene was dried by reflux over sodium wire and was then freshly distilled into a dry receiver under nitrogen. Dibutyl ether was dried over sodium wire, distilled, and redistilled from LiAlH<sub>4</sub> immediately before use.

Commercial nitro compounds, nitrosobenzene and 2-nitrosotoluene were recrystallised or distilled before use.

2-Nitroso-5-phenoxytoluene **3k** was prepared from 4-phenoxy nitrobenzene and methylmagnesium chloride according to our procedure.<sup>17</sup> Other nitrosoarenes were synthesized by Lutz's procedure.<sup>18</sup>

1-(Trimethylsilyl)vinylmagnesium bromide **2a** and 1-(trimethylsilyl)vinyl lithium were prepared, according to the literature method,<sup>10</sup> in THF solution, then, when necessary, the solvent was removed under reduced pressure. Freshly distilled, dry dibutyl ether was added through a septum with a syringe until a homogeneous solution was obtained.

*Reaction between Nitroso Derivatives and 1-(Trimethylsilyl)vinylmagnesium Bromide.*—To a vigorously stirred, nitrogen-flushed solution of Grignard reagent (12 mmol) in Bu<sub>2</sub>O at -50 °C was added dropwise a solution of a nitrosoarene (5 mmol) in the same solvent (10 cm<sup>3</sup>). After 10 min the mixture was allowed to warm to 0 °C and was then kept at this temperature overnight. The reaction mixture was then quenched with saturated aq. ammonium chloride, then extracted with diethyl ether, and the extract was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure, and the residue was submitted to flash chromatography on a silica gel column [light petroleum (b.p. 40–60 °C)–diethyl ether (9:1) as eluent].

In order to improve the reaction yield, 2-nitrosotoluene was allowed to react under the different reaction conditions reported in Table 2.

Azo and azoxy derivatives were recognised by comparison with authentic samples prepared according to literature methods.<sup>19</sup>

Yields are reported in Table 1; physical data of new compounds follow.

2-(Trimethylsilyl)indole **8da**: oil (Found: C, 69.75; H, 8.0; N, 7.4. C<sub>11</sub>H<sub>15</sub>NSi requires C, 69.8; H, 8.0; N, 7.4%);  $\delta_{\text{H}}$  0.37 (9 H, s, SiMe<sub>3</sub>), 6.67 (1 H, d, *J* 2, 3-H), 7.00–7.67 (4 H, m, ArH) and 8.33 (1 H, br, NH);  $\nu_{\text{max}}$ (CCl<sub>4</sub>)/cm<sup>-1</sup> 3414 (NH) and 1250 (CSi); *m/z* 189 (M<sup>+</sup>), 175, 174 (100%), 158, 130, 117, 87, 73 and 43.

4-Methyl-2-(trimethylsilyl)indole **8ba**: oil (Found: C, 70.8; H, 8.4; N, 7.0. C<sub>12</sub>H<sub>17</sub>NSi requires C, 70.9; H, 8.4; N, 6.9%);  $\delta_{\text{H}}$  0.30 (9 H, s, SiMe<sub>3</sub>), 2.50 (3 H, s, Me), 6.67 (1 H, d, 3-H), 6.73–7.20 (3 H, m, ArH) and 8.00 (1 H, br, NH);  $\nu_{\text{max}}$ (CCl<sub>4</sub>)/cm<sup>-1</sup> 3479 (NH) and 1250 (CSi); *m/z* 203 (M<sup>+</sup>), 188 (100%), 172, 144, 115, 94, 59 and 43.

**5-Methyl-2-(trimethylsilyl)indole 8ca:** oil (Found: C, 70.9; H, 8.45; N, 6.9%);  $\delta_{\text{H}}$  0.33 (9 H, s, SiMe<sub>3</sub>), 2.43 (3 H, s, Me), 6.50 (1 H, d, *J* 1.5, 4-H), 6.73–7.20 (2 H, AB, 6- and 7-H), 7.23 (1 H, d, *J* 1.5, 3-H) and 7.83 (1 H, br, NH);  $\nu_{\text{max}}(\text{CCl}_4)/\text{cm}^{-1}$  3480 (NH) and 1250 (CSi); *m/z* 203 (M<sup>+</sup>), 188 (100%), 160, 144, 130, 94, 73 and 43.

**6-Methyl-2-(trimethylsilyl)indole 8b'a:** oil (Found: C, 70.8; H, 8.45; N, 6.9%);  $\delta_{\text{H}}$  0.30 (9 H, s, SiMe<sub>3</sub>), 2.37 (3 H, s, Me), 6.60 (1 H, d, 3-H), 6.73–7.20 (2 H, m, ArH), 7.45 (1 H, d, *J* 8, 4-H) and 8.00 (1 H, br, NH);  $\nu_{\text{max}}(\text{CCl}_4)/\text{cm}^{-1}$  3479 (NH) and 1250 (CSi); *m/z* 203 (M<sup>+</sup>, 100%), 188, 172, 160, 115, 73, 59 and 43.

**7-Methyl-2-(trimethylsilyl)indole 8aa:** oil (Found: C, 70.9; H, 8.45; N, 6.9%);  $\delta_{\text{H}}$  0.37 (9 H, s, SiMe<sub>3</sub>), 2.50 (3 H, s, Me), 6.68 (1 H, d, *J* 2, 3-H), 6.87–7.53 (3 H, m, ArH) and 8.00 (1 H, br, NH);  $\nu_{\text{max}}(\text{CCl}_4)/\text{cm}^{-1}$  3482 (NH) and 1251 (CSi); *m/z* 203 (M<sup>+</sup>), 189, 188 (100%), 160, 130, 115, 94, 77 and 43.

**4-Chloro-2-(trimethylsilyl)indole 8fa:** oil (Found: C, 58.9; H, 6.35; N, 6.3. C<sub>11</sub>H<sub>14</sub>ClNSi requires C, 59.0; H, 6.3; N, 6.3%);  $\delta_{\text{H}}$  0.36 (9 H, s, SiMe<sub>3</sub>), 6.77 (1 H, d, *J* 2, 3-H), 6.93–7.30 (3 H, m, ArH) and 8.33 (1 H, br, NH);  $\nu_{\text{max}}(\text{CCl}_4)/\text{cm}^{-1}$  3476 (NH) and 1250 (CSi); *m/z* 225 (M<sup>+</sup> + 2), 223 (M<sup>+</sup>), 210, 208 (100%), 172, 170, 130, 105, 73, 63 and 43.

**5-Chloro-2-(trimethylsilyl)indole 8ga:** oil (Found: C, 59.0; H, 6.3; N, 6.35%);  $\delta_{\text{H}}$  0.33 (9 H, s, SiMe<sub>3</sub>), 6.58 (1 H, d, *J* 2, 3-H) and 6.90–7.57 (4 H, m, ArH + NH);  $\nu_{\text{max}}(\text{CCl}_4)/\text{cm}^{-1}$  3478 (NH) and 1251 (CSi); *m/z* 225 (M<sup>+</sup> + 2), 223 (M<sup>+</sup>), 210, 208 (100%), 130, 104 and 43.

**6-Chloro-2-(trimethylsilyl)indole 8fa:** oil (Found: C, 58.9; H, 6.3; N, 6.4%);  $\delta_{\text{H}}$  0.33 (9 H, s, SiMe<sub>3</sub>), 6.67 (1 H, d, *J* 2, 3-H), 7.00 (1 H, dd, *J* 8 and 2, 5-H), 7.33 (1 H, d, *J* 2, 7-H), 7.5 (1 H, d, *J* 8, 4-H) and 8.20 (1 H, br, NH);  $\nu_{\text{max}}(\text{CCl}_4)/\text{cm}^{-1}$  3476 (NH) and 1251 (CSi); *m/z* 225 (M<sup>+</sup> + 2), 223 (M<sup>+</sup>), 210, 208 (100%), 182, 180, 172, 144, 130, 104, 63 and 43.

**7-Chloro-2-(trimethylsilyl)indole 8ea:** oil (Found: C, 59.0; H, 6.2; N, 6.3%);  $\delta_{\text{H}}$  0.33 (9 H, s, SiMe<sub>3</sub>), 6.67 (1 H, d, *J* 2, 3-H), 6.93–7.53 (3 H, m, ArH) and 8.37 (1 H, br, NH);  $\nu_{\text{max}}(\text{CCl}_4)/\text{cm}^{-1}$  3472 (NH) and 1250 (CSi); *m/z* 225 (M<sup>+</sup> + 2), 223 (M<sup>+</sup>), 210, 208 (100%), 192, 172, 130, 104, 93 and 63.

**7-Bromo-2-(trimethylsilyl)indole 8ha:** oil (Found: C, 49.3; H, 5.2; N, 5.2. C<sub>11</sub>H<sub>14</sub>BrNSi requires C, 49.3; H, 5.3; N, 5.2%);  $\delta_{\text{H}}$  0.37 (9 H, s, SiMe<sub>3</sub>), 6.73 (1 H, d, *J* 2, 3-H), 6.90 (1 H, t, *J* 8, 5-H), 7.30 (1 H, dd, *J* 1 and 8, ArH), 7.50 (1 H, dd, *J* 1 and 8, ArH) and 8.17 (1 H, br, NH);  $\nu_{\text{max}}(\text{CCl}_4)/\text{cm}^{-1}$  3468 (NH) and 1250 (CSi); *m/z* 269 (M<sup>+</sup> + 2), 267 (M<sup>+</sup>), 254 (100%), 252, 188, 172, 130, 115, 73 and 43.

**7-Ethyl-2-(trimethylsilyl)indole 8ia:** oil (Found: C, 71.9; H, 8.8; N, 6.45. C<sub>13</sub>H<sub>19</sub>NSi requires C, 71.8; H, 8.8; N, 6.4%);  $\delta_{\text{H}}$  0.33 (9 H, s, SiMe<sub>3</sub>), 1.30 (3 H, t, *J* 7, Me), 2.83 (2 H, q, CH<sub>2</sub>), 6.70 (1 H, d, *J* 1.5, 3-H), 6.90–7.57 (3 H, m, ArH) and 8.00 (1 H, br, NH);  $\nu_{\text{max}}(\text{CCl}_4)/\text{cm}^{-1}$  3481 (NH) and 1250 (CSi); *m/z* 217 (M<sup>+</sup>, 100%), 202, 174, 158, 130, 94, 73 and 59.

**5,7-Dichloro-2-(trimethylsilyl)indole 8ja:** oil (Found: C, 51.5; H, 5.05; N, 5.4. C<sub>11</sub>H<sub>13</sub>Cl<sub>2</sub>NSi requires C, 51.2; H, 5.1; N, 5.4%);  $\delta_{\text{H}}$  0.36 (9 H, s, SiMe<sub>3</sub>), 6.70 (1 H, d, *J* 2, 3-H), 7.20 (1 H, d, *J* 1.5, 6-H), 7.50 (1 H, d, *J* 1 and 5, 4-H) and 8.20 (1 H, br, NH);  $\nu_{\text{max}}(\text{CCl}_4)/\text{cm}^{-1}$  3470 (NH) and 1251 (CSi); *m/z* 261 (M<sup>+</sup> + 4), 259 (M<sup>+</sup> + 2), 257 (M<sup>+</sup>), 246, 244, 242 (100%), 209, 207, 164, 122, 93, 73 and 63.

**7-Methyl-5-phenoxy-2-(trimethylsilyl)indole 8ka:** oil (Found: C, 73.1; H, 7.2; N, 4.7. C<sub>18</sub>H<sub>21</sub>NOSi requires C, 73.2; H, 7.2; N, 4.7%);  $\delta_{\text{H}}$  0.35 (9 H, s, SiMe<sub>3</sub>), 2.50 (3 H, s, Me), 6.67 (1 H, d, *J* 2, 3-H), 6.73–7.50 (7 H, m, ArH) and 8.00 (1 H, br, NH);  $\nu_{\text{max}}(\text{CCl}_4)/\text{cm}^{-1}$  3479 (NH), 1253 (CSi) and 1223 (C–O); *m/z* 295 (M<sup>+</sup>, 100%), 280, 187, 172, 77, 73 and 45.

**7-Methyl-2-phenylindole 8ab** had m.p. 117 °C (lit.,<sup>20</sup> 117–118 °C).

**Reaction between Nitro Derivatives and 1-(Trimethylsilyl)-vinylmagnesium Bromide.**—NH<sub>4</sub>Cl quenching. To a stirred THF solution of a nitroarene (5 mmol, 10 cm<sup>3</sup>) at 0 °C flushed with nitrogen was added dropwise a solution of a Grignard reagent (15 mmol, 30 cm<sup>3</sup>). After 10 min the mixture was quenched with saturated aq. ammonium chloride and extracted with diethyl ether, the extract was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure, and the residue was submitted to flash chromatography on a silica gel column [light petroleum (b.p. 40–60 °C)–diethyl ether (9:1) as eluent]. The following products were isolated and characterised.

**7-Methyl-2-(trimethylsilyl)indole 8aa** (12%).

**2-Methyl-4-[1-(trimethylsilyl)vinyl]nitrobenzene 12aa** (9%), oil (Found: C, 61.3; H, 7.3; N, 5.8. C<sub>12</sub>H<sub>17</sub>NO<sub>2</sub>Si requires C, 61.2; H, 7.3; N, 5.9%);  $\delta_{\text{H}}$  0.20 (9 H, s, SiMe<sub>3</sub>), 2.67 (3 H, s, Me), 5.70–5.97 (2 H, AB, =CH<sub>2</sub>), 7.03–7.30 (2 H, m, 3- and 5-H) and 8.00 (1 H, d, *J* 9, 6-H);  $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$  1517, 1344 (NO<sub>2</sub>) and 1251 (CSi); *m/z* 235 (M<sup>+</sup>), 220, 205, 194, 115, 73 (100%) and 45.

**5-Methoxy-2-(trimethylsilyl)indole 8ma** (18%), oil (Found: C, 65.6; H, 7.85; N, 6.4. C<sub>12</sub>H<sub>17</sub>NOSi requires C, 65.7; H, 7.8; N, 6.4%);  $\delta_{\text{H}}$  0.30 (9 H, s, SiMe<sub>3</sub>), 3.87 (3 H, s, OMe), 6.83 (1 H, d, *J* 2, 3-H), 6.80–7.33 (3 H, m, ArH) and 8.80 (1 H, br, NH);  $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$  3410 (NH) and 1252 (CSi); *m/z* 219 (M<sup>+</sup>, 100%), 204, 189, 174, 159, 95 and 73.

**2-Methyl-4-(1-phenylvinyl)nitrobenzene 12ab** (8%), oil (Found: C, 75.4; H, 5.5; N, 5.9. C<sub>15</sub>H<sub>13</sub>NO<sub>2</sub> requires C, 75.3; H, 5.5; N, 5.8%);  $\delta_{\text{H}}$  2.63 (3 H, s, Me), 5.43–5.83 (2 H, AB, =CH<sub>2</sub>), 7.1–7.73 (7 H, m, ArH) and 8.1 (1 H, d, *J* 9, 6-H);  $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$  1518 and 1345 (NO<sub>2</sub>); *m/z* 239 (M<sup>+</sup>, 100%), 223, 193, 178, 165, 120, 103, 77 and 51.

**DDQ quenching.** To a stirred THF solution of a nitroarene (5 mmol, 10 cm<sup>3</sup>) at 0 °C, flushed with nitrogen, was added dropwise a solution of a Grignard reagent (11 mmol, 25 cm<sup>3</sup>). After 10 min a THF solution of DDQ (12 mmol, 30 cm<sup>3</sup>) was added dropwise. After 2 h the mixture was poured into 5% aq. acetic acid, then extracted with diethyl ether, the organic layer was washed with aq. NaHCO<sub>3</sub> dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated under reduced pressure, and the residue was submitted to flash chromatography on a silica gel column [light petroleum (b.p. 40–60 °C)–diethyl ether (9:1) as eluent]. Isolated products and yields are listed in Table 3; physical data of new compounds follow.

**2-Methyl-6-(1-phenylvinyl)nitrobenzene 13ab:** oil (Found: C, 75.2; H, 5.4; N, 5.9. C<sub>15</sub>H<sub>13</sub>NO<sub>2</sub> requires C, 75.3; H, 5.5; N, 5.8%);  $\delta_{\text{H}}$  2.37 (3 H, s, Me), 5.43–5.83 (2 H, AB, =CH<sub>2</sub>) and 7.1–7.73 (8 H, m, ArH);  $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$  1518 and 1345 (NO<sub>2</sub>); *m/z* 239 (M<sup>+</sup>), 222, 180 (100%), 165, 105, 77 and 51.

**2-Methyl-6-[1-(trimethylsilyl)vinyl]nitrobenzene 13aa:** oil (Found: C, 61.3; H, 7.25; N, 5.8. C<sub>12</sub>H<sub>17</sub>NO<sub>2</sub>Si requires C, 61.2; H, 7.3; N, 5.9%);  $\delta_{\text{H}}$  0.20 (9 H, s, SiMe<sub>3</sub>), 2.40 (3 H, s, Me), 5.60–5.83 (2 H, AB, =CH<sub>2</sub>) and 6.67–7.43 (3 H, m, ArH);  $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$  1531, 1370 (NO<sub>2</sub>) and 1251 (CSi); *m/z* 220 (M<sup>+</sup> – 15), 218, 175, 146, 115, 91, 75, 73 (100%) and 45.

**2-Methoxy-1-nitro-4-[1-(trimethylsilyl)vinyl]naphthalene 12oa:** oil (Found: C, 63.9; H, 6.35; N, 4.65. C<sub>16</sub>H<sub>19</sub>NO<sub>3</sub>Si requires C, 63.8; H, 6.3; N, 4.6%);  $\delta_{\text{H}}$  0.17 (9 H, s, SiMe<sub>3</sub>), 4.07 (3 H, s, OMe), 5.83–6.13 (2 H, AB, =CH<sub>2</sub>), 6.90 (1 H, s, 3-H) and 7.23–7.97 (4 H, m, ArH);  $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$  1530, 1355 (NO<sub>2</sub>) and 1250 (CSi); *m/z* 301 (M<sup>+</sup>), 286, 271, 255, 161, 152, 139, 75 and 73 (100%).

**2,6-Dimethyl-4-[1-(trimethylsilyl)vinyl]nitrobenzene 12na:** oil (Found: C, 62.5; H, 7.7; N, 5.5. C<sub>13</sub>H<sub>19</sub>NO<sub>2</sub>Si requires C, 62.6; H, 7.7; N, 5.6%);  $\delta_{\text{H}}$  0.20 (9 H, s, SiMe<sub>3</sub>), 2.40 (6 H, s, Me), 5.63–5.90 (2 H, AB, =CH<sub>2</sub>) and 6.90 (2 H, s, ArH);  $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$  1524, 1367 (NO<sub>2</sub>) and 1250 (CSi); *m/z* 249 (M<sup>+</sup>), 219, 173, 160, 130, 73 (100%) and 45.

**2-Methoxy-4-[1-(trimethylsilyl)vinyl]nitrobenzene 12la:** oil (Found: C, 57.2; H, 6.9; N, 5.6. C<sub>12</sub>H<sub>17</sub>NO<sub>3</sub>Si requires C, 57.3;

H, 6.8; N, 5.6%);  $\delta_{\text{H}}$  0.18 (9 H, s, SiMe<sub>3</sub>), 3.97 (3 H, s, OMe), 5.67–5.91 (2 H, AB, =CH<sub>2</sub>), 6.68–6.90 (2 H, m, ArH) and 7.83 (1 H, d, *J* 9, 6-H);  $\nu_{\text{max}}$ (film)/cm<sup>-1</sup> 1516, 1347 (NO<sub>2</sub>) and 1250 (CSi); *m/z* 251 (M<sup>+</sup>), 246, 221, 210, 189, 163, 131, 102, 75, 73 (100%) and 45.

2-Methoxy-6-[1-(trimethylsilyl)vinyl]nitrobenzene **13la**: oil (Found: C, 57.4; H, 6.9; N, 5.6%);  $\delta_{\text{H}}$  0.11 (9 H, s, SiMe<sub>3</sub>), 3.92 (3 H, s, OMe), 5.67–5.91 (2 H, AB, =CH<sub>2</sub>), 6.55–6.97 (2 H, m, ArH) and 7.33 (1 H, dd, *J* 8 and 9, 4-H);  $\nu_{\text{max}}$ (film)/cm<sup>-1</sup> 1516, 1347 (NO<sub>2</sub>) and 1250 (CSi); *m/z* 251 (M<sup>+</sup>), 236, 218, 191, 162, 133, 75 and 73 (100%).

4-Methoxy-2-[1-(trimethylsilyl)vinyl]nitrobenzene **13ma**: oil (Found: C, 57.2; H, 6.8; N, 5.5%);  $\delta_{\text{H}}$  0.10 (9 H, s, SiMe<sub>3</sub>), 3.88 (3 H, s, OMe), 5.63 (2 H, s, =CH<sub>2</sub>), 6.50 (1 H, d, *J* 3, 3-H), 6.80 (1 H, dd, 5-H) and 8.07 (1 H, d, *J* 9, 6-H);  $\nu_{\text{max}}$ (film)/cm<sup>-1</sup> 1512, 1340 (NO<sub>2</sub>) and 1247 (CSi); *m/z* 251 (M<sup>+</sup>), 236, 191, 162, 133, 73 (100%) and 45.

The reaction of 4-nitroanisole was also carried out in 1,2-dimethoxyethane as solvent. 4-Methoxy-2-[1-(trimethylsilyl)vinyl]nitrobenzene **13ma** was recovered in 20% yield.

The reaction of 4-nitroanisole was also carried out in THF at -70 °C, followed by oxidation with DDQ at 0 °C for 2 h. 4-Methoxy-2-[1-(trimethylsilyl)vinyl]nitrobenzene **13ma** was recovered in 15% yield.

The reaction of 4-nitroanisole was also carried out in THF at reflux, followed by oxidation with DDQ at the same temperature for 1 h. 4-Methoxy-2-[1-(trimethylsilyl)vinyl]nitrobenzene **13ma** was recovered in 25% yield.

#### Acknowledgements

This work was supported by a grant from the Italian C.N.R. Progetto Chimica Fine II.

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Paper 1/02704B

Received 6th June 1991

Accepted 18th June 1991