



## Reaction of Dianions of Acyclic $\beta$ -Enamino Ketones with Electrophiles. 8<sup>(a)</sup>. Synthesis of Trialkylsilylenaminones and $\alpha'$ -Silylated $\beta$ -Diketones

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**Abstract:**  $\alpha'$ - and  $\gamma$ -Dianions of  $\beta$ -(monoalkylamino)  $\alpha,\beta$ -unsaturated ketones react with trialkylchlorosilanes leading to  $\alpha'$ - and  $\gamma$ -trialkylsilylenaminones. Conversely from trimethylchlorosilane, the reaction between dianions of 3-(*N*-isopropylamino)-1-arylbut-2-en-1-ones and *t*-butyldimethylchlorosilane or triisopropylchlorosilane leads to the corresponding 4-trialkylsilyl derivatives. An explanation of these findings is reported. Hydrolysis of these compounds affords the until now unknown  $\alpha'$  silylated  $\beta$ -diketones. Copyright © 1996 Elsevier Science Ltd

In the last few years we set up the optimum conditions for the  $\alpha'$ - and  $\gamma$ -dimetallation of  $\beta$ -(monoalkylamino)  $\alpha,\beta$ -unsaturated ketones<sup>1</sup> (enaminones). Both dianions react with a large variety of electrophiles such as alkyl halides,<sup>1</sup> oxiranes,<sup>2</sup> nitriles,<sup>3</sup> aldehydes and ketones,<sup>4</sup> esters,<sup>5</sup> nitroalkenes,<sup>6</sup> carbon dioxide and carbonates.<sup>7</sup>

However, non-carbon electrophiles were not tested except in a preliminary manner. In our previous paper, we reported that arylenaminones react with trimethylchlorosilane in the presence of an excess of base to give arylalkynyl ketones,<sup>8</sup> while silylated enaminones are not isolable.

In this paper we report that the silylation of enaminones is feasible and that by hydrolysis of the obtained silylated derivatives the until now unknown  $\alpha'$ -silylated 1,3-diketones have been prepared.

### Results and Discussion

The reaction of 1-phenyl-3-(*N*-isopropylamino)but-2-en-1-one (**1a**) with two equivalents of lithium 2,2,6,6-tetramethylpiperidide (LTMP)<sup>7</sup> followed by the addition of *t*-butyldimethylchlorosilane (**3a**) or triisopropylchlorosilane (**3b**) led to the corresponding  $\gamma$ -silylated products **4aa** and **4ab** in very good yields (Table 1, entries 1,2). Arylalkynylketones or imines were never detected.

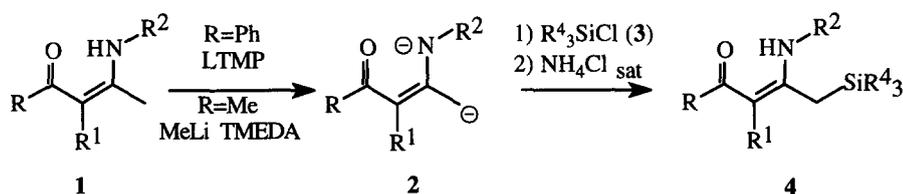
*N*-Phenyl (**1b**) or  $\alpha$ -substituted (**1c**) arylenaminones can be silylated at the  $\gamma$ -position with trimethylchlorosilane (**3c**) (Table 1, entries 4,5), although compound **4bc** cannot be isolated since it gives starting enaminone when heated or chromatographed on silica gel. However, <sup>1</sup>H-NMR analysis of the crude

mixture revealed almost exclusively signals belonging to **1b** and **4bc**. It should be noted that carrying out the reaction of **2a** with **3c** starting enaminone was recovered in 94% yield.<sup>8</sup>

Good yields of products **4** were obtained, when  $\gamma$ -dianions of 4-(*N*-monoalkylamino)pent-3-en-2-one **2d-f**, prepared by reaction of enaminones **1d-f** with two equivalents of methylolithium in the presence of tetramethylethylenediamine (TMEDA),<sup>1</sup> were allowed to react with **3a** (Table 1, entries 6,7,8). Attempts to synthesize both the corresponding  $\gamma$ -trimethylsilyl derivatives **4ec-fc** and pent-3-yn-2-one were unsuccessful, the starting enaminone being the sole isolable and detectable product. On the other hand, 4-(*N*-phenylamino)-5-(trimethylsilyl)pent-3-en-2-one was isolated and characterized, but it could not be stored since it rapidly decomposed.

These findings demonstrate that  $\gamma$ -silylation of enaminones is feasible so that silylated intermediates can be supposed to be involved in the reaction pathway of  $\alpha,\beta$ -alkynyl ketone formation as depicted in the scheme.

**Table 1**- Reaction of  $\gamma$ -Dianions **2** of Enaminones with Trialkylchlorosilanes **3** at Room Temperature, Followed by Quenching with Saturated Ammonium Chloride.



Entry	Dianion	R	R <sup>1</sup>	R <sup>2</sup>	R <sup>4</sup> <sub>3</sub> SiCl ( <b>3</b> )	R <sup>4</sup> <sub>3</sub>	Product	Yield <sup>a</sup> (%)
1	<b>2a</b>	Ph	H	Pr <sup>i</sup>	<b>3a</b>	Bu <sup>t</sup> Me <sub>2</sub>	<b>4aa</b>	70
2	<b>2a</b>	Ph	H	Pr <sup>i</sup>	<b>3b</b>	Pr <sup>i</sup> <sub>3</sub>	<b>4ab</b>	97
3	<b>2a</b>	Ph	H	Pr <sup>i</sup>	<b>3c</b>	Me <sub>3</sub>	<b>4ac</b>	0 <sup>b</sup>
4	<b>2b</b>	Ph	H	Ph	<b>3c</b>	Me <sub>3</sub>	<b>4bc</b>	48 <sup>c</sup>
5	<b>2c</b>	Ph	CH <sub>2</sub> Ph	Pr <sup>i</sup>	<b>3c</b>	Me <sub>3</sub>	<b>4cc</b>	68 <sup>d</sup>
6	<b>2d</b>	Me	H	Me	<b>3a</b>	Bu <sup>t</sup> Me <sub>2</sub>	<b>4da</b>	77
7	<b>2e</b>	Me	H	Pr <sup>i</sup>	<b>3a</b>	Bu <sup>t</sup> Me <sub>2</sub>	<b>4ea</b>	71
8	<b>2f</b>	Me	H	Ph	<b>3a</b>	Bu <sup>t</sup> Me <sub>2</sub>	<b>4fa</b>	85
9	<b>2f</b>	Me	H	Ph	<b>3c</b>	Me <sub>3</sub>	<b>4fc</b>	46 <sup>e</sup>

<sup>a</sup> Calculated on pure isolated products.

<sup>b</sup> Starting enaminone **1a** was recovered in 94% yield.<sup>8</sup>

<sup>c</sup> Estimated on NMR signals on the crude reaction mixture.

<sup>d</sup> About 18% of starting material **1c** was recovered.

<sup>e</sup> 72% GC-yield before isolation. After column chromatography 25% of starting material **1f** was recovered.

In the scheme, dianion **2** is shown in its more stable conformation as derived from *ab initio* calculations.<sup>1</sup> It is reasonable to assume that phenyl and very bulky nitrogen substituents hamper the rotation around the pseudo-single C2-C3 bond, avoiding the oxygen and silicon atoms facing each other, so stabilising the  $\gamma$ -silylated product. In fact, the same nitrogen substituents affect the  $\alpha'$ - $\gamma$  equilibration which occurs with a similar mechanism.<sup>1</sup> In this conformation the silylated monoanion undergoes bond-switching from the  $\gamma$ -silylated **5** to the *O*-silylated isomer **6**.

It is noteworthy that  $\beta$ -diketone monosilylenoethers exhibit a similar bond-switching with a calculated activation energy of *ca.* 55 kJ mol<sup>-1</sup>.<sup>9</sup> Although the present rearrangement involves oxygen and carbon atoms rather than two oxygen atoms, the termini of the rearrangement are facing each other. The equilibrium between **5** and **6** isomers seems to be shifted toward the *C*-silylated form, especially when the silicon atom is very hindered.

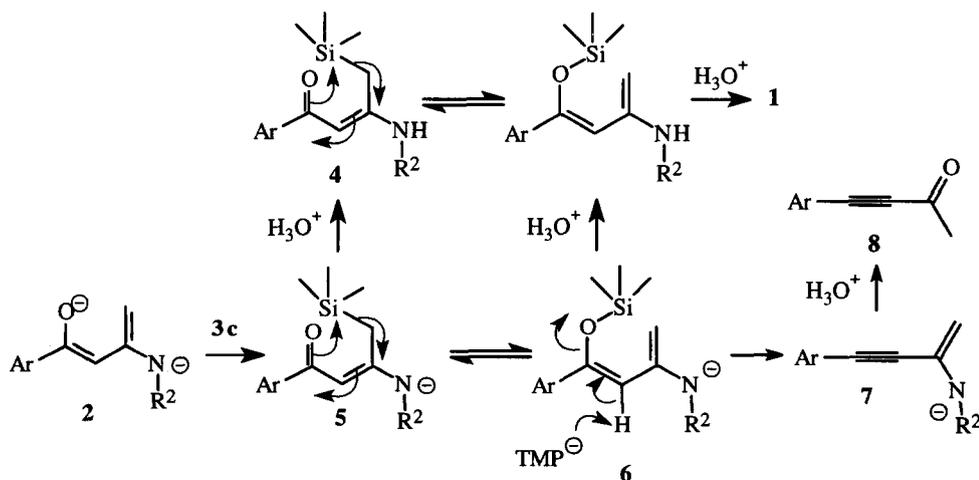
The reaction of 2-benzyl-1-phenyl-3-(*N*-isopropylamino)but-2-en-1-one (**1c**) with trimethylchlorosilane can be assumed as a photo of this equilibrium. 18% Yield of starting enaminone is recovered also in the presence of five equivalents of LTMP. This finding cannot be explained in terms of transmetalation from dianion **2c** to silylated monoanion **5cc**, since the excess of base should give dianion **2c** again. Therefore the presence of starting material can be only accounted for by hydrolysis of the *O*-silylated product **6cc**.

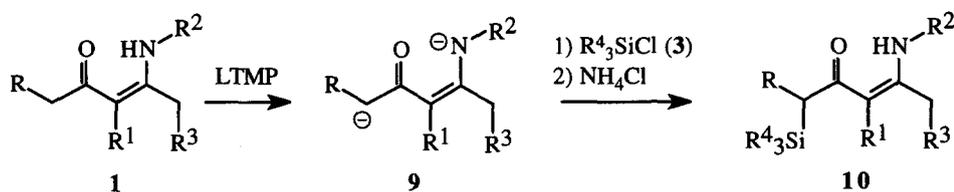
Bond-switching might occur also in compound **4** and from hydrolysis of the *O*-silylated product during the quenching of the reaction mixture, the starting material can be restored, so justifying its recovery from workup of the reactions.

If excess base is present, a silanol elimination can be promoted from **6** to alkynyl monoanion **7** which hydrolyses to alkynylketone after acidic workup of the reaction mixture.<sup>8</sup> When both an alkyl substituent is present in the  $\alpha$  position, and bulky *N*-substituents prevent bond-switching, no alkynyl derivatives are observed and the corresponding  $\gamma$ -silylated products are detected.

The role of the aryl substituents on the C-1 atom is obscure, but probably they can better stabilize the incipient positive charge than an alkyl group.

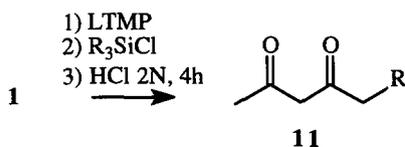
Scheme



**Table 2-** Reaction of  $\alpha'$ -Dianions **9** of Enaminones with Trialkylchlorosilanes **3** at Room Temperature, Followed by Quenching with Saturated Ammonium Chloride.

Entry	Dianion	R	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup> <sub>3</sub> SiCl	R <sup>4</sup> <sub>3</sub>	Product	Yield <sup>a</sup> (%)
1	<b>9e</b>	H	H	Pr <sup>i</sup>	H	<b>3a</b>	Bu <sup>t</sup> Me <sub>2</sub>	<b>10ea</b>	74
2	<b>9e</b>	H	H	Pr <sup>i</sup>	H	<b>3c</b>	Me <sub>3</sub>	<b>10ec</b>	78
3	<b>9f</b>	H	H	Ph	H	<b>3a</b>	Bu <sup>t</sup> Me <sub>2</sub>	<b>10fa</b>	85
4	<b>9f</b>	H	H	Ph	H	<b>3c</b>	Me <sub>3</sub>	<b>10fc</b>	79
5	<b>9g</b>	H	H	Ph	Bu	<b>3c</b>	Me <sub>3</sub>	<b>10gc</b>	52
6	<b>9h</b>	Bu	H	Ph	H	<b>3c</b>	Me <sub>3</sub>	<b>10hc</b>	48

<sup>a</sup> Calculated on pure isolated products.

**Table 3-** Hydrolysis of Silylated Enaminones with 2N Hydrochloric Acid.

Entry	Enaminone	R <sub>3</sub> SiCl	R	Diketone	Yield (%) <sup>a</sup>
1	<b>1e</b>	<b>3a</b>	Bu <sup>t</sup> Me <sub>2</sub> Si	<b>11a</b>	66
2	<b>1f</b>	<b>3a</b>	Bu <sup>t</sup> Me <sub>2</sub> Si	<b>11a</b>	78
3	<b>1e</b>	<b>3c</b>	H	<b>11b</b>	72

<sup>a</sup> Calculated on pure isolated products

Product **4fc** is stable for some hours after isolation, although it partially decomposes during chromatographic separation. On the other hand, product **4bc** cannot be isolated and its presence in the reaction mixture was proved by TLC and NMR analyses on the crude.

The reaction was then extended to the  $\alpha'$  dianions, generated under the optimum conditions for their generation.<sup>1</sup> The reaction proceeds smoothly and the corresponding  $\alpha'$ -silylated products **10** are obtained in good to high yields (Table 2).

It is noteworthy that the  $\alpha'$ -trimethylsilylenaminones are isolable and stable under 0 °C for months, conversely from the corresponding  $\gamma$ - derivatives.

The enamino function was submitted to hydrolysis under the reported conditions.<sup>10</sup> All the reactions were carried out both on isolated products **4** and **10** and on the reaction mixture. Following the reaction course by GC-MS analysis we found that after 4 h the  $\gamma$ -isomers are hydrolyzed to starting enaminones with every silyl substituent. This finding confirms a lower stability of  $\gamma$ -isomers. On the other hand, the  $\alpha'$ -*t*-butyldimethylsilyl derivatives afford the corresponding unknown  $\alpha'$ -silylated enaminones, while the trimethylsilyl group is hydrolyzed (table 3).

In conclusion, a new class of silylated  $\beta$ -diketones and enaminones is now available. They can be valuable intermediates for the synthesis of  $\alpha',\beta'$ -unsaturated enaminones and diketones, *via* their dianion reaction with aldehydes or ketones, which cannot be prepared by reaction of enaminones with carbonyl derivatives<sup>4</sup>. Moreover they can be used to prepare  $\gamma,\delta$ -unsaturated ketones by cerium mediated addition<sup>11</sup> of alkyl lithium followed by Peterson elimination.

Studies are in progress to explore these synthetic applications.

### Experimental

<sup>1</sup>H-NMR spectra were recorded with a Bruker AW80 instrument or with a Varian Gemini 200 instrument. Chemical shifts are given in p.p.m. from Me<sub>4</sub>Si as external standard in CDCl<sub>3</sub> solutions. Coupling constants are given in Hertz. IR spectra were recorded with a Perkin-Elmer FTIR paragon 1000 PC spectrometer. EI-MS were recorded with a workstation formed by an HP-5890 gaschromatograph equipped with a methyl silicone capillary column and by an HP 5975 mass detector. Melting points are uncorrected and were determined with a Kofler apparatus. THF was dried by refluxing over sodium wire until the blue colour of benzophenone ketyl persisted and then distilling into a dry receiver under a nitrogen atmosphere.

Enaminones **1a-f,i** were prepared according to Singh and Tandon's procedure.<sup>12</sup> Enaminones **1g,h** were prepared from **1a** and the appropriate halide according to our procedure.<sup>1</sup> LTMP was prepared from equimolecular amounts of butyllithium and 2,2,6,6-tetramethylpiperidine in THF at 0 °C. Dianions **2** and **9** were prepared as previously described.<sup>1</sup> 3-Benzyl-2,4-pentandione and 2-benzyl-1-phenyl-1-butanone, were prepared according to literature<sup>13</sup>.

All reactions were performed in a 5 mmol scale.

#### *Reaction of dianions 2 with trialkylchlorosilanes 3.*

To a magnetically stirred THF solution of dianion **2** (1 M) a twofold amount of trialkylchlorosilane was added dropwise at 0 °C. After 30 min, the reaction was quenched with an ammonium chloride saturated aqueous solution, extracted with Et<sub>2</sub>O, dried over sodium sulphate, evaporated under reduced pressure and submitted to a chromatographic separation on silica gel (hexane : ethyl acetate 95:5 as eluant). The following products were isolated. Yields are reported in table 1.

*3-(N-isopropylamino)-1-phenyl-4-(tertbutyldimethylsilyl)but-2-en-1-one 4aa.* mp 87-88 °C.  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 0.10 (s, 6H, Me<sub>2</sub>Si); 0.95 (s, 9H, Me<sub>3</sub>C); 1.30 (d, *J*=6.4, 6H, Me<sub>2</sub>CH); 1.91 (s, 2H, CH<sub>2</sub>Si); 3.70 (dhept, 1H, CHNH); 5.48 (s, 1H, CH=); 7.38 (m, 3H, ArH); 7.85 (m, 2H ArH), 11.75 (brd, *J*=8, 1H, NH). IR (KBr)  $\nu_{\text{max}}$

1252 (CSi)  $\text{cm}^{-1}$ .  $m/z$  (%) 317 ( $\text{M}^+$ , 29), 316 (100), 274 (17), 218 (11), 202 (4), 73 (20), 42 (10). Anal calcd for  $\text{C}_{19}\text{H}_{31}\text{NOSi}$  C, 71.9; H, 9.8; N, 4.4. Found C, 71.9; H, 9.7; N, 4.5%.

*3-(N-isopropylamino)-1-phenyl-4-(triisopropylsilyl)but-2-en-1-one 4ab*. Oil.  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 1.03 (m, 18H,  $\text{Me}_2\text{CHSi}$ ); 1.11 (m, 3H,  $\text{CHSi}$ ); 1.28 (d,  $J=6.4$ , 6H,  $\text{Me}_2\text{CHN}$ ); 2.08 (s, 2H,  $\text{CH}_2\text{Si}$ ); 3.79 (dhept, 1H,  $\text{CHNH}$ ); 5.60 (s, 1H,  $\text{CH=}$ ); 7.37 (m, 3H,  $\text{ArH}$ ); 7.84 (m, 2H,  $\text{ArH}$ ); 11.43 (brd,  $J=8.7$ , 1H,  $\text{NH}$ ).  $m/z$  (%) 359 ( $\text{M}^+$ , 31), 358 (110), 316 (22), 274 (34), 207 (14), 188 (16), 115 (10), 83 (38), 73 (18), 59 (28), 42 (36). Anal calcd for  $\text{C}_{22}\text{H}_{37}\text{NOSi}$  C, 73.5; H, 10.4; N, 3.9. Found C, 73.7; H, 10.3; N, 3.9%.

*3-(N-phenylamino)-1-phenyl-4-(trimethylsilyl)but-2-en-1-one 4bc*. Not isolable.  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 0.03 (s, 9H,  $\text{Me}_3\text{Si}$ ); 2.05 (s, 2H,  $\text{CH}_2\text{Si}$ ); 5.75 (s, 1H,  $\text{CH=}$ ); 7.20-7.50 and 7.80-8.00 (m, 8H+2H,  $\text{ArH}$ ); 13.40 (brs, 1H,  $\text{NH}$ ).

*2-benzyl-3-(N-isopropylamino)-1-phenyl-4-(trimethylsilyl)but-2-en-1-one 4cc*. Oil.  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 0.20 (s, 9H,  $\text{Me}_3\text{Si}$ ); 1.47 (d,  $J=6.5$ , 6H,  $\text{Me}_2\text{CHN}$ ); 2.08 (s, 2H,  $\text{CH}_2\text{Si}$ ); 2.90-3.10 (AB, 2H,  $\text{CH}_2\text{Ph}$ ); 3.98 (dhept, 1H,  $\text{CHNH}$ ); 7.20-7.50 (m, 10H,  $\text{ArH}$ ); 13.20 (brd,  $J=10.5$ , 1H,  $\text{NH}$ ). IR (film)  $\nu_{\text{max}}$  1249 (CSi)  $\text{cm}^{-1}$ .  $m/z$  (%) 365 ( $\text{M}^+$ , 3), 322 (12), 105 (10), 84 (77), 73 (31), 42 (100). Anal calcd for  $\text{C}_{23}\text{H}_{31}\text{NOSi}$  C, 75.6; H, 8.6; N, 3.8. Found C, 75.7; H, 8.5; N, 3.9%.

*4-(N-methylamino)-5-(tertbutyldimethylsilyl)pent-3-en-2-one 4da*. Oil.  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 0.03 (s, 6H,  $\text{Me}_2\text{Si}$ ); 0.86 (s, 9H,  $\text{Me}_3\text{C}$ ); 1.86 (s, 2H,  $\text{CH}_2\text{Si}$ ); 1.94 (s, 3H,  $\text{MeCO}$ ); 2.88 (d,  $J=5.25$ , 3H,  $\text{MeNH}$ ); 4.93 (s, 1H,  $\text{CH=}$ ); 10.70 (brq, 1H,  $\text{NH}$ ). IR (film)  $\nu_{\text{max}}$  1250 (CSi)  $\text{cm}^{-1}$ .  $m/z$  (%) 227 ( $\text{M}^+$ , 1), 212 (14), 170 (21), 156 (100), 73 (18), 56 (24). Anal calcd for  $\text{C}_{12}\text{H}_{25}\text{NOSi}$  C, 63.4; H, 11.1; N, 6.2. Found C, 63.2; H, 11.1; N, 6.1%.

*4-(N-isopropylamino)-5-(tertbutyldimethylsilyl)pent-3-en-2-one 4ea*. Oil.  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 0.03 (s, 6H,  $\text{Me}_2\text{Si}$ ); 0.86 (s, 9H,  $\text{Me}_3\text{C}$ ); 1.17 (d,  $J=6.4$ , 6H,  $\text{Me}_2\text{CH}$ ); 1.89 (s, 2H,  $\text{CH}_2\text{Si}$ ); 1.93 (s, 3H,  $\text{MeCO}$ ); 3.70 (dhept, 1H,  $\text{CHNH}$ ); 4.85 (s, 1H,  $\text{CH=}$ ); 10.80 (brd, 1H,  $\text{NH}$ ). IR (film)  $\nu_{\text{max}}$  1254 (CSi)  $\text{cm}^{-1}$ .  $m/z$  (%) 255 ( $\text{M}^+$ , 1), 240 (16), 156 (100), 73 (20), 42 (11). Anal calcd for  $\text{C}_{14}\text{H}_{29}\text{NOSi}$  C, 65.8; H, 11.4; N, 5.5. Found C, 66.0; H, 11.3; N, 5.5%.

*4-(N-phenylamino)-5-(tertbutyldimethylsilyl)pent-3-en-2-one 4fa*. Oil.  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 0.08 (s, 6H,  $\text{Me}_2\text{Si}$ ); 0.90 (s, 9H,  $\text{Me}_3\text{C}$ ); 1.98 (s, 3H,  $\text{MeCO}$ ); 2.01 (s, 2H,  $\text{CH}_2\text{Si}$ ); 5.03 (s, 1H,  $\text{CH=}$ ); 7.00-7.40 (m, 5H,  $\text{ArH}$ ); 12.38 (brs, 1H,  $\text{NH}$ ). IR (film)  $\nu_{\text{max}}$  1255 (CSi)  $\text{cm}^{-1}$ .  $m/z$  (%) 289 ( $\text{M}^+$ , 17), 274 (31), 232 (88), 218 (15), 198 (11), 156 (91), 141 (100), 117 (64), 77 (58), 75 (67). Anal calcd for  $\text{C}_{17}\text{H}_{27}\text{NOSi}$  C, 70.5; H, 9.4; N, 4.8. Found C, 70.6; H, 9.3; N, 4.7%.

*4-(N-phenylamino)-5-(trimethylsilyl)pent-3-en-2-one 4fc*. Oil.  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 0.10 (s, 9H,  $\text{Me}_3\text{Si}$ ); 1.98 (s, 3H,  $\text{MeCO}$ ); 2.03 (s, 2H,  $\text{CH}_2\text{Si}$ ); 5.01 (s, 1H,  $\text{CH=}$ ); 7.00-7.40 (m, 5H,  $\text{ArH}$ ); 12.40 (brs, 1H,  $\text{NH}$ ). IR (film)  $\nu_{\text{max}}$  1251 (CSi)  $\text{cm}^{-1}$ .  $m/z$  (%) 247 ( $\text{M}^+$ , 54), 232 (78), 175 (7), 156 (48), 132 (12), 118 (29), 73 (100). Anal calcd for  $\text{C}_{14}\text{H}_{21}\text{NOSi}$  C, 68.0; H, 8.6; N, 5.7. Found C, 67.9; H, 8.6; N, 5.7%.

#### *Reaction of dianions 9 with trialkylchlorosilanes 3.*

To a magnetically stirred THF solution of dianion **9** (1 M) a twofold amount of trialkylchlorosilane was added dropwise at 0 °C. After 30 min, the reaction was quenched with an ammonium chloride saturated aqueous solution, extracted with  $\text{Et}_2\text{O}$ , dried over sodium sulphate, evaporated under reduced pressure and submitted to a chromatographic separation on silica gel (hexane : ethyl acetate 95:5 as eluant). The following products were isolated. Yields are reported in table 2.

*4-(N-isopropylamino)-1-(tertbutyldimethylsilyl)pent-3-en-2-one 10ea*. Oil.  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 0.05 (s, 6H,  $\text{Me}_2\text{Si}$ ); 0.84 (s, 9H,  $\text{Me}_3\text{C}$ ); 1.16 (d,  $J=6.4$ , 6H,  $\text{Me}_2\text{CH}$ ); 1.85 (s, 2H,  $\text{CH}_2\text{CO}$ ); 1.87 (s, 3H, 5-Me); 3.70 (dhept, 1H,  $\text{CHNH}$ ); 4.71 (s, 1H;  $\text{CH=}$ ); 10.56 (d,  $J=6.6$ ; 1H;  $\text{NH}$ ). IR (film)  $\nu_{\text{max}}$  1253 ( $\text{CSi}$ )  $\text{cm}^{-1}$ .  $m/z$  (%) 255 ( $\text{M}^+$ , 2), 198 (100), 156 (81), 124 (42), 73 (42), 42 (58). Anal calcd for  $\text{C}_{14}\text{H}_{29}\text{NOSi}$  C, 65.8; H, 11.4; N, 5.5. Found C, 65.9; H, 11.3; N, 5.5%.

*4-(N-isopropylamino)-1-(trimethylsilyl)pent-3-en-2-one 10ec*. Oil.  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 0.04 (s, 9H,  $\text{Me}_3\text{Si}$ ); 1.16 (d,  $J=6.4$ , 6H,  $\text{Me}_2\text{CH}$ ); 1.87 (s, 2H,  $\text{CH}_2\text{CO}$ ); 1.88 (s, 3H, 5-Me); 3.65 (dhept, 1H,  $\text{CHNH}$ ); 4.70 (s, 1H,  $\text{CH=}$ ); 10.54 (brd,  $J=6.6$ , 1H,  $\text{NH}$ ). IR (film)  $\nu_{\text{max}}$  1245 ( $\text{CSi}$ )  $\text{cm}^{-1}$ .  $m/z$  (%) 213 ( $\text{M}^+$ , 29), 198 (51), 156 (37), 126 (61), 108 (29), 98 (28), 84 (38), 73 (84), 58 (19), 42 (100). Anal calcd for  $\text{C}_{11}\text{H}_{23}\text{NOSi}$  C, 62.0; H, 10.9; N, 6.6. Found C, 61.9; H, 11.0; N, 6.5%.

*4-(N-phenylamino)-1-(tertbutyldimethylsilyl)pent-3-en-2-one 10fa*. Oil.  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 0.07 (s, 6H,  $\text{Me}_2\text{Si}$ ); 0.89 (s, 9H,  $\text{Me}_3\text{C}$ ); 1.99 (s, 3H, 5-Me); 2.01 (s, 2H,  $\text{CH}_2\text{Si}$ ); 5.03 (s, 1H,  $\text{CH=}$ ); 7.00-7.40 (m, 5H,  $\text{ArH}$ ); 12.35 (brs, 1H,  $\text{NH}$ ). IR (film)  $\nu_{\text{max}}$  1250 ( $\text{CSi}$ )  $\text{cm}^{-1}$ .  $m/z$  (%) 289 ( $\text{M}^+$ , 5), 232 (41), 156 (76), 141 (98), 118 (44), 77 (85), 73 (100), 43 (30). Anal calcd for  $\text{C}_{17}\text{H}_{27}\text{NOSi}$  C, 70.5; H, 9.4; N, 4.8. Found C, 70.4; H, 9.5; N, 4.8%.

*4-(N-phenylamino)-1-(trimethylsilyl)pent-3-en-2-one 10fc*. Oil.  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 0.10 (s, 9H,  $\text{Me}_3\text{Si}$ ); 1.99 (s, 3H, 5-Me); 2.03 (s, 2H,  $\text{CH}_2\text{Si}$ ); 5.01 (s, 1H,  $\text{CH=}$ ); 7.00-7.40 (m, 5H,  $\text{ArH}$ ); 12.35 (brs, 1H,  $\text{NH}$ ). IR (film)  $\nu_{\text{max}}$  1258 ( $\text{CSi}$ )  $\text{cm}^{-1}$ .  $m/z$  (%) 247 ( $\text{M}^+$ , 7), 228 (11), 156 (11), 118 (12), 77 (30), 73 (100), 45 (28), 43 (13). Anal calcd for  $\text{C}_{14}\text{H}_{21}\text{NOSi}$  C, 68.0; H, 8.6; N, 5.7. Found C, 68.2; H, 8.6; N, 5.6%.

*4-(N-phenylamino)-1-(trimethylsilyl)non-3-en-2-one 10gc*. Oil.  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 0.00 (s, 9H,  $\text{Me}_3\text{Si}$ ); 0.70 (t, 3H,  $J=7$ ,  $\text{MeCH}_2$ ); 1.07-1.10 (m, 4H); 1.25-1.35 (m, 2H); 1.93 (s, 2H,  $\text{CH}_2\text{Si}$ ); 2.15 (t, 2H,  $J=7.5$ ,  $\text{CH}_2\text{C=}$ ); 4.91 (s, 1H,  $\text{CH=}$ ); 6.95-7.30 (m, 5H,  $\text{ArH}$ ); 12.20 (brs, 1H,  $\text{NH}$ ). IR (film)  $\nu_{\text{max}}$  1267 ( $\text{CSi}$ )  $\text{cm}^{-1}$ .  $m/z$  (%) 303 ( $\text{M}^+$ , 12), 288 (31), 260 (43), 247 (42), 232 (67), 211 (23), 156 (28), 77 (27), 73 (100), 43 (24). Anal calcd for  $\text{C}_{18}\text{H}_{29}\text{NOSi}$  C, 71.3; H, 9.6; N, 4.6. Found C, 71.1; H, 9.5; N, 4.7%.

*2-(N-phenylamino)-5-(trimethylsilyl)non-2-en-4-one 10hc*. Oil.  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 0.00 (s, 9H,  $\text{Me}_3\text{Si}$ ); 0.81 (t, 3H,  $J=7$ ,  $\text{MeCH}_2$ ); 1.10-1.35 (m, 6H); 1.90-2.01 (m, 1H,  $\text{CHSi}$ ); 1.96 (s, 3H, 1-Me); 4.97 (s, 1H,  $\text{CH=}$ ); 7.00-7.30 (m, 5H,  $\text{ArH}$ ); 12.45 (brs, 1H,  $\text{NH}$ ). IR (film)  $\nu_{\text{max}}$  1263 ( $\text{CSi}$ )  $\text{cm}^{-1}$ .  $m/z$  (%) 303 ( $\text{M}^+$ , 19), 288 (14), 260 (100), 211 (49), 160 (33), 118 (66), 77 (54), 73 (80), 43 (18). Anal calcd for  $\text{C}_{18}\text{H}_{29}\text{NOSi}$  C, 71.3; H, 9.6; N, 4.6. Found C, 71.5; H, 9.5; N, 4.6%.

*Reaction of dianions 2 and 9 with trialkylchlorosilanes 3 followed by hydrolysis of the enamino function.*

To a magnetically stirred THF solution of dianions **2a** and **2e** (1 M) a twofold amount of **3a** was added dropwise at 0 °C. After 30 min, the reaction was quenched with 20 mL of 2 N hydrochloric acid and allowed to stir at room temperature. Every 30 min, reaction mixture samples were submitted to GC-MS analysis and the peak of products **4aa** and **4ea** decreased while peaks of enamines **1a** and **1e** increased.

To a magnetically stirred THF solution of dianions **9e** and **9f** (1 M) a twofold amount of **3a** was added dropwise at 0 °C. After 30 min, the reaction was quenched with 20 mL of 2 N hydrochloric acid and allowed to stir at room temperature for 4 h, neutralized with solid sodium carbonate, extracted with  $\text{Et}_2\text{O}$ , dried over sodium sulphate, evaporated under reduced pressure and submitted to a chromatographic separation on silica gel (hexane : ethyl acetate 95:5 as eluant). Yields are reported in table 3.

*1-(tertbutyldimethylsilyl)-4-hydroxy-3-penten-2-one 11a*. Oil. keto:enol 1:9.6.  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 0.05 (s, 9H,  $\text{Me}_2\text{Si}$ ); 0.90 (s, 9H,  $\text{Me}_3\text{C}$ ); 1.93 (s, 2H,  $\text{CH}_2\text{Si}$  enol); 1.99 (s, 3H, 5-Me enol); 2.24 (s, 3H, 5-Me keto); 2.30 (s, 2H,  $\text{CH}_2\text{Si}$  keto); 3.52 (s, 2H,  $\text{COCH}_2\text{CO}$ ); 5.35 (s, 1H,  $\text{CH}=\text{C}$ ); 12.05 (brs, 1H, OH). IR (film)  $\nu_{\text{max}}$  1254 ( $\text{CSi}$ )  $\text{cm}^{-1}$ .  $m/z$  (%) 199 ( $\text{M}^+-15$ , 2), 157 (77), 139 (11), 114 (15), 75 (100); 43 (26). Anal calcd for  $\text{C}_{11}\text{H}_{22}\text{O}_2\text{Si}$  C, 61.6; H, 10.3. Found C, 61.5; H, 10.4%.

Under the same experimental conditions the reaction between **9e** and **3c** led to 2,4-pentandione which was recognized by comparison with an authentic sample.

### References and Notes

- a. Part 7: see ref. 7
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(Received in UK 11 April 1996; revised 15 May 1996; accepted 16 May 1996)