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# 2-Aza-1,3-Dienes : Methods of Synthesis and Stereochemical Studies ‡

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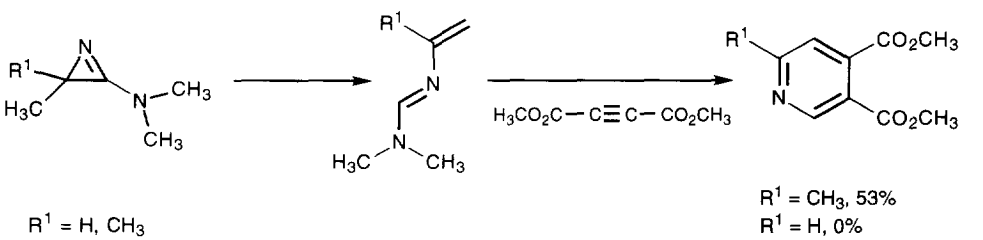
***Abstract*** *:* 2-Aza-1,3-dienes bearing an activating trialkylsilyloxy group at C-3 have been prepared via three routes. The first route involves the silylation of N-acylimidates which are readily available from iminoether hydrochlorides and acid chlorides. According to a more general route towards these doubly activated dienes, N-trialkylsilylimidates and N-trialkylsilylimines derived from non-enolizable aldehydes were conveniently converted in a one-pot sequence into the corresponding azadienes by reaction with an acid chloride in the presence of triethylamine. Finally, cyclic dienes could be prepared by direct silylation of glutarimide on both oxygens with trialkylsilyltriflate in the presence of triethylamine. The configuration and conformation of 2-azadienes have been established by $^{1}H$, $^{13}C$ and $^{15}N$ NMR spectroscopy.

## INTRODUCTION

The design and preparation of highly functionalized dienes have made the venerable Diels-Alder reaction an extraordinarily useful tool for the synthesis of 6-membered carbocycles. Several recent reviews[1] have brought to light the spectacular progresses made in the development of new heterodienes which are of practical use for the preparation of 6-membered heterocycles.

In 1975, Dr A. Demoulin in our group[2] discovered an unexpected reaction leading to N-vinylamidines (Scheme 1).




$R^1$ = H, $CH_3$

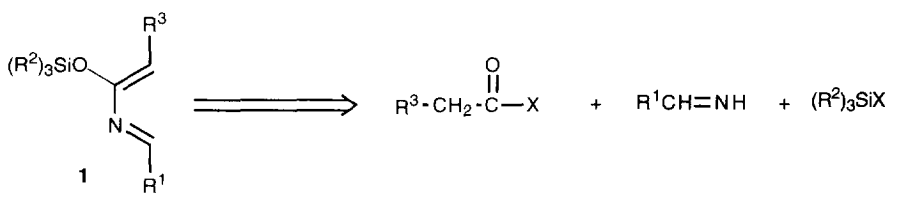
$R^1$ = $CH_3$, 53%
$R^1$ = H, 0%

Scheme 1

‡ Dedicated to Professor R. Neidlein on the occasion of his 65th birthday.

These compounds were shown to react efficiently as 2-aza-1,3-dienes with electron-deficient dienophiles when $R^1$ was different from hydrogen. When $R^1$ = H, a fast reaction took place leading to a complex mixture which did not contain any cycloadduct. Thus, it appeared that when the s-cis conformation was less populated ($R^1$ = H), a competing reaction took place involving the electrophilic dienophile and the nucleophilic nitrogen of the amidine group. Further studies have confirmed the crucial role of conformational factors on the enophilic properties of azadienes.[3]

With these considerations in mind, we felt that 2-aza-1,3-dienes **1** bearing a trialkylsilyloxy group at C-3 should fulfil all the requirements to undergo hetero Diels-Alder reactions with electron-poor dienophiles. First, the population of the s-cis conformation should be increased by the presence of a substituent at C-3. Then, the electron-donating character of the silyloxy group will increase the energy of the HOMO of the diene and its coefficient at C-4, thus favouring an attack of the dienophile on that position. Moreover, the silylenol ether function is a masked carbonyl group which can be regenerated after the cycloaddition, allowing for further transformations. These functionalized 2-aza-1,3-dienes should be readily accessible by a convergent process combining a carboxylic acid synthon with an imine synthon (Scheme 2).



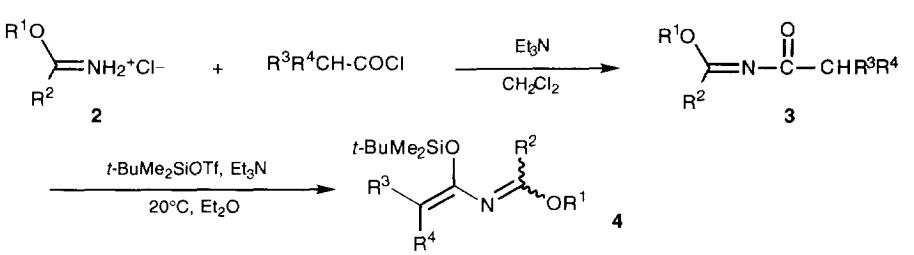
Scheme 2

In preliminary communications,[3b,4] we have already demonstrated the high reactivity of azadienes **1** in Diels-Alder reactions. Herein, we describe the full details of their synthesis and a study of their configuration and conformation.

## SYNTHESIS

*1. from iminoethers:*

1,3-Diactivated 2-aza-1,3-dienes **4** can be easily obtained by a general method involving the acylation of the readily available iminoether hydrochlorides **2** followed by silylation of the resulting acylimidates **3** (Scheme 3).



Scheme 3 (method A)

Iminoether hydrochlorides **2** can be prepared by the Pinner synthesis[5] or by the reaction of an amide with an alcohol in the presence of benzoyl chloride.[6] The latter method was preferred when $R^2$ = H since it avoids the use of HCN. The free bases derived from **2** ($R^2$ = H) are known to readily trimerize when $R^1$ = Me, Et. For this reason, we preferred to use the more stable isopropyl derivative ($R^1$ = *i*-Pr, $R^2$ = H).

The acylation of iminoether hydrochlorides **2** with acid chlorides in the presence of triethylamine has been described for $R^2 \neq H$.[7] We have applied this method to the preparation of a series of new acylimidates **3** (Table 1, Method A). When $R^2$ = H, the acylation had to be carried out at -40° C to avoid the trimerization of the iminoether. With the more stable acetimidate ($R^2$ = Me) or benzimidate ($R^2$ = Ph), the acylation was carried out at room temperature. Compounds **3** were obtained in good yields after purification by bulb-to-bulb distillation.

The silylation of **3** gave satisfactory yields of the corresponding azadienes **4** (Table 1, Method A) which were purified by bulb-to-bulb distillation without significant loss of material.

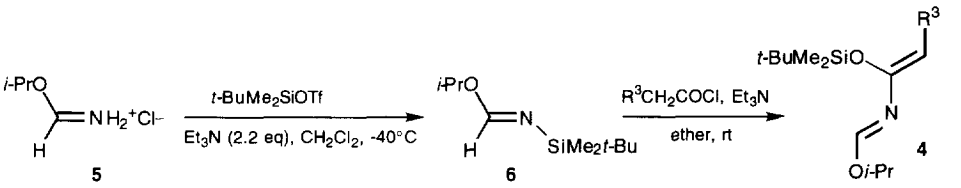
Table 1 : Yields of N-acyliminoethers **3** and 2-aza-1,3-dienes **4**.

| Entry | $R^1$ | $R^2$ | $R^3$ | $R^4$ | Method A | | Method B |
|---|---|---|---|---|---|---|---|
| | | | | | Yield of **3** (%) | Yield of **4** (%) | Yield of **4** (%) |
| a | *i*-$C_3H_7$ | H | H | H | 76 | 77 | 74 |
| b | *i*-$C_3H_7$ | H | $CH_3$ | H | 70 | 74 | 77 |
| c | *i*-$C_3H_7$ | H | *n*-$C_4H_9$ | H | 66 | 70 | - |
| d | *i*-$C_3H_7$ | H | $C_6H_5$ | H | 75 | 82 | 76 |
| e | *i*-$C_3H_7$ | H | $C_6H_5CH_2$ | H | 73 | 81 | 73 |
| f | *i*-$C_3H_7$ | H | $C(CH_3)_3$ | H | 72 | 65[a] | 70 |
| g | *i*-$C_3H_7$ | H | $CH=CH_2$ | H | 52 | 0 | 80 |
| h | *i*-$C_3H_7$ | H | F | H | 73 | 79[b] | 55[b,c] |
| i | *i*-$C_3H_7$ | H | Cl | H | 63 | 69[d] | 73 |
| j | *i*-$C_3H_7$ | H | $CH_3$ | $CH_3$ | 63 | 90 | - |
| k | *i*-$C_3H_7$ | H | $COOCH_3$ | H | 0 | - | 71[e] |
| l | *i*-$C_3H_7$ | H | $ArCH_2$[f] | H | - | - | 83[g] |
| m | $C_2H_5$ | $CH_3$ | H | H | 83 | 91 | - |
| n | $C_2H_5$ | $CH_3$ | $CH_3$ | H | 87 | 74 | - |
| o | $CH_3$ | $C_6H_5$ | H | H | 72 | 73 | - |

*a*: compound contaminated with 25% of **3f**; *b*: mixture of *Z:E* (70:30) isomers; *c*: the reaction affords also 24 % of acylimidate **3h**; *d*: mixture of *Z:E* (85:15) isomers; *e*: mixture of *Z:E* (80:20) isomers; *f*: Ar=m,p-(dimethoxyphenyl)-; *g*: compound contaminated with 5% of acylimidate.

This method failed when applied to the preparation of 2-azadienes **4g** and **4k** bearing a vinyl or a methyl ester group at carbon 4. Acylimidate **3k** could not be prepared whereas acylimidate **3g** was obtained in moderate yield but could not be converted into azadiene **4g**. Another route has been developed to overcome these difficulties: 2-azadienes **4** could be even more conveniently prepared by reversing the reactions' sequence. Compound **6** was prepared by treatment of iminoether hydrochloride **5** with one equivalent of t-butyldimethylsilyl triflate in the presence of 2.2 equivalents of triethylamine at - 40° C in dichloromethane. The crude N-silyl iminoether was clean and was used as such because it decomposed during distillation (Scheme 4).

Addition of one equivalent of acid chloride to a mixture of the silylated iminoether **6** and triethylamine in dry ether gave the azadienes **4**. In most cases, an excess of triethylamine had to be be used in order to observe a complete conversion of the silylated iminoether into azadienes (see details in the Experimental Section). The reactions were over after two hours at room temperature (Table 1, Method B).

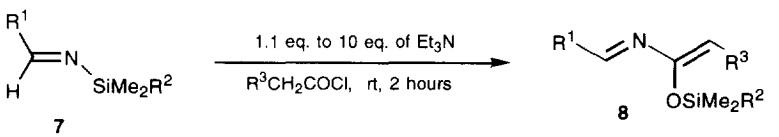



Scheme 4 (method B)

Both methods A and B involve the same number of steps starting from isopropylformimidate hydrochloride **5**. The yields of 2-azadienes are similar. However, method B is advantageous because all the dienes are obtained in one step from the same precursor **6**. Moreover, this sequence could also be applied to the synthesis of dienes **4g** and **4k** which could not be prepared by method A.

*2. from imines :*

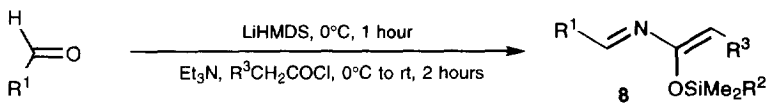
3-Trialkylsilyloxy-2-aza-1,3-dienes bearing an alkyl or an aryl substituent at C-1 could also be prepared using method B (Scheme 5). N-Silylimines have been prepared following known procedures.[8,9] Acylation of **7** with one equivalent of acid chloride in the presence of triethylamine yielded azadienes **8** (Scheme 5 and Table 2, Method B). In most cases (see Experimental Section), an excess of triethylamine was needed for completion of the reaction. It is worth mentioning that strong bases such as DBU, *t*-BuOLi, *t*-BuOK, LiHMDS and LDA were inefficient. This method appears to be fairly general but does not apply to the formation of azadienes bearing an electron-withdrawing group at C-1 (Table 2, entries u and v). It was also unsuccessful for the preparation of diene **8p**.




Scheme 5 (method B)

*3. from aldehydes :*

We have examined whether it was possible to by-pass the isolation of N-silylated imines **7** and developed a one-pot conversion of aldehydes into 2-azadienes. This was accomplished by treatment of the aldehyde with LiHMDS to give the imines **7** followed by acylation in the presence of triethylamine (Scheme 6 and Table 2, Method C). Although the yields are slightly lower than those of method B, the one-pot procedure (Method C) is more practical when applied to non-enolisable aldehydes. Indeed, with the exception of isobutyraldehyde (entries r and s), enolisable aldehydes could not be transformed into 2-azadienes by method C.




Scheme 6 (method C)

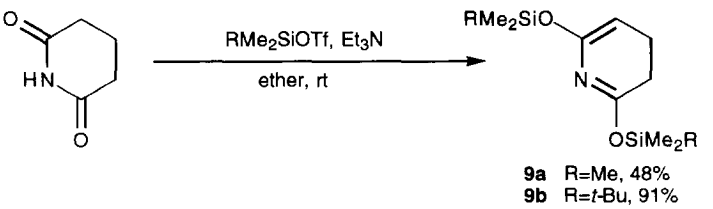
Table 2 : Synthesis of 3-trialkylsilyloxy-2-aza-1,3-dienes **8**.

| Entry | $R^1$ | $R^2$ | $R^3$ | Method B Yield of **8** (%) | Method C Yield of **8** (%) |
|---|---|---|---|---|---|
| a | Ph | Me | H | 72 (59[a]) | 50 |
| b | Ph | Me | Me | 67 (57[a])[c] | 50 |
| c | Ph | Me | $CH=CH_2$ | 67 | - |
| d | Ph | Me | Ph | 96[b] (79[a]) | 95 |
| e | Ph | Me | *t*-Bu | 86 | - |
| f | Ph | *t*-Bu | H | 65 | - |
| g | Ph | *t*-Bu | Me | 70[c] | - |
| h | *t*-Bu | Me | H | 70 | - |
| i | *t*-Bu | Me | Me | 66 | - |
| j | *t*-Bu | Thexyl | H | 65 | - |
| k | 2-furyl | Me | H | 68 (54[a]) | 50 |
| l | 2-furyl | Me | Me | 71 (57[a])[c] | 49 |
| m | 2-furyl | Me | Ph | 97[b] | - |
| n | 2-furyl | *t*-Bu | H | 64 | - |
| o | PhCH=CH | Me | Ph | 90[b] | 51[b] |
| p | PhCH=CH | Me | H | 0 | 27[b] |
| q | PhCH=CMe | Me | Ph | - | 78[b] |
| r | $CH(CH_3)_2$ | Me | Me | - | 30[c] |
| s | $CH(CH_3)_2$ | Me | Ph | - | 25 |
| t | $CH_2=CMe$ | Me | Me | - | 35 |
| u | $CO_2Et$ | *t*-Bu | H | 0 | - |
| v | $CF_3$ | *t*-Bu | Me | 0 | - |

*a:* overall yield calculated from the aldehyde; *b*: crude compound; *c*: the reaction affords a mixture of isomers (*Z*:*E* > 90:10).

*4. from imides :*

Cyclic azadienes **9a** and **9b** have been prepared by direct silylation of glutarimide on both oxygen atoms with trialkylsilyl triflates in the presence of triethylamine (Scheme 7).[10]




**9a** R=Me, 48%
**9b** R=*t*-Bu, 91%

Scheme 7

The combination of trialkylsilyl chlorides with zinc chloride and triethylamine[11] appeared to be less efficient and led to monosilylated products. Bulb-to-bulb distillation of azadiene **9a** bearing a trimethylsilyloxy group was always accompanied by considerable loss of material. On the other hand, azadiene **9b** bearing the bulkier t-butyldimethylsilyloxy substituent was more stable and could be easily purified by distillation. We also found that azadienes prepared with trialkylsilyl triflates contained traces of triflic acid even after careful distillation. If needed, the residual acid could be removed by adding a small amount of trimethyl-3-propenylsilane. Also, an acid free diene could be obtained by reacting glutarimide with two equivalents of LDA at -78° C and quenching the resulting dianion with t-butyldimethylsilyl chloride.

## PROPERTIES OF 2-AZADIENES

We have thus developed several practical methods for the synthesis of a new class of heterodienes. After distillation, these compounds are pure enough to be employed in Diels-Alder reactions. They are sensitive to moisture and air and must be kept under inert atmosphere at dry ice temperature. They decompose slowly at room temperature. As a consequence, no satisfactory elemental analyses could be obtained. However, NMR spectra generally showed a purity of $\geq 95\%$.

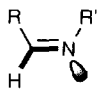
For most reactions, only one stereoisomer was obtained as demonstrated by $^1H$ NMR on the crude mixtures. We observed only one set of signals for protons positioned on carbons 1 and 4. For dienes obtained as mixtures of stereoisomers around the carbon-carbon or the carbon-nitrogen double bond, two sets of signals were observed. From Tables 1 and 2, we can make the following observations : monoactivated 2-azadienes **8** bearing a trialkylsilyloxy group on position 3 were all obtained as single stereoisomers except for **8b**, **8g**, **8l** and **8r**. On the other hand, azadienes **4h**, **4i** (Method A) and **4k** bearing two activating electron-donating groups at positions 1 and 3 and one electron-withdrawing group at position 4 were obtained as mixtures of *Z* and *E* isomers. The *Z* isomer was always largely predominant.

## STEREOCHEMISTRY

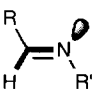
The knowledge of the configuration of the C=C and C=N double bonds as well as the conformation of the diene system is essential to the understanding of the stereochemical course of the cycloadditions of 2-azadienes to olefins. They have been unambiguously assigned using $^1H$, $^{13}C$ and $^{15}N$ NMR spectroscopy for a series of representative 2-azadienes.

***Configuration of the C=N bond :***

A reliable NMR parameter for the configurational assignment of the C=N double bond of 2-azadienes is the geminal coupling constant $^2J_{NH}$.[12] It is well-known that the $^2J_{NH}$ shows a high negative value (-10 to -15 Hz) when the lone pair of the nitrogen atom is in a cis relationship with respect to the hydrogen (*Z* isomer). A small positive value (2 to 5 Hz) is usually observed when the lone pair is trans with respect to the hydrogen (*E* isomer) (Scheme 8).




*Z* isomer
$^2J_{NH}$ = -10 to -15 Hz




*E* isomer
$^2J_{NH}$ = +2 to +5 Hz

Scheme 8

In the case of 2-azadienes (Scheme 10, Table 3), the $^2J_{NH}$ coupling constants are always smaller than 5 Hz in support for a *E* configuration for the C=N bond.

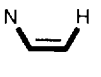
Table 3 : $^2J_{NH}$, $^3J_{NH}$, $^3J_{NH'}$ for selected azadienes

| Azadiene | $R^1$ | $R^2$ | $R^3$ | $^2J_{NH}$ (Hz) | $^3J_{NH}$ (Hz) | $^3J_{NH'}$ (Hz) |
|---|---|---|---|---|---|---|
| **4a** | O*i*-Pr | *t*-Bu | H' | 2.2 | 2.2 | 5.8 |
| **4d** | O*i*-Pr | *t*-Bu | Ph | 1.8 | *a* | - |
| **4e** | O*i*-Pr | *t*-Bu | $CH_2Ph$ | 1.8 | 0.7 | - |
| **8a** | Ph | Me | H' | 3.7 | 2.5 | 6.9 |
| **8b** | Ph | Me | Me | 4.0 | 2.4 | - |
| **8c** | Ph | Me | $-CH=CH_2$ | 3.8 | 2.3 | - |
| **8 h** | *t*-Bu | Me | H' | 4.1 | 2.1 | 6.0 |

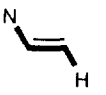
*a:* unresolved broad singlet.

***Configuration of the C=C bond :***

The vicinal $^3J_{NH}$ coupling constants through the $\pi$ bond of enamines and related compounds have been shown to depend on the relative configuration of the coupled nuclei :[13] a cis relationship between the N and H atoms corresponds to a small coupling constant (≤ 3 Hz), while a trans relationship gives values ranging from 3.5 Hz to 7 Hz (Scheme 9).



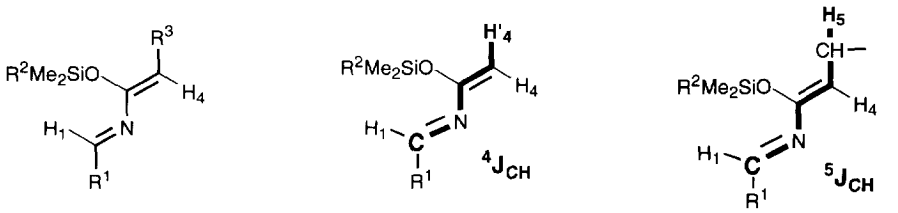

$^3J_{NH}$ ≤ 3 Hz




$^3J_{NH}$ = 3.5-7 Hz

Scheme 9

Both coupling constants are observed in the $^{15}N$ NMR spectra of azadienes **4a**, **8a** and **8h** which bear two hydrogens at C-4 (Table 3). On the other hand, azadienes **4d**, **e** and **8b**, **c** which bear only one hydrogen at C-4 show a small $^{3}J_{NH}$ coupling constant. This is in agreement with a *Z* configuration around the C=C bond of these azadienes.




Scheme 10

***Conformation :***

The conformation of 2-azadienes was deduced from the long range $^{4}J_{CH}$ and $^{5}J_{CH}$ coupling constants (Scheme 10, Table 4). Only W arrangements shown in Scheme 10 give an observable long range coupling.[14]

For all azadienes bearing no substituent at C-4, selective irradiation revealed a $^{4}J_{CH}$ coupling constant between $C_1$ and $H'_4$. This is consistent with a W arrangement between these nuclei and support a s-trans conformation for the azadiene backbone.

Table 4 : $^{4}J_{CH}$ values for selected azadienes

| Azadiene | $R^1$ | $R^2$ | δC1 (ppm) | $^{4}J_{CH}$ (Hz) |
|---|---|---|---|---|
| **4a** | O*i*-Pr | *t*-Bu | 154.4 | 1.3 |
| **8a** | Ph | Me | 155.9 | 1.7 |
| **8h** | *t*-Bu | Me | 168.8 | 0.9 |
| **8f** | Ph | *t*-Bu | 156.2 | 1.1 |
| **8j** | *t*-Bu | Thexyl | 169.1 | 0.9 |
| **8k** | 2-furyl | Me | 144.2 | 1.2 |
| **8n** | 2-furyl | *t*-Bu | 143.7 | 1.2 |

As expected from these observations, azadienes bearing a substituent at C-4 showed no $^{4}J_{CH}$. However, a $^{5}J_{C1\text{-}H5}$ coupling constant was observed by selective irradiation of the terminal methyl or benzylic protons. All these observations agree with a s-trans conformation of the azadiene backbone and *E* configuration around the C=N bond and a *Z* configuration around the C=C bond. In one case (Table 1, 4k), we could also analyse the $^{13}C$ NMR spectra of the crude minor diastereoisomer which was formed in the synthesis. In that case, a $^{4}J_{C1\text{-}H4}$ coupling constant of ± 1.5 Hz was observed. This observation agrees very well with an *E* configuration around the C=C bond and a s-trans conformation for the diene backbone.

## CONCLUSION

We have thus shown that a large variety of 2-azadienes can be prepared by simple, practical and convergent methods from an imine and carboxylic acid synthons. As already shown in preliminary reports, they should find a wide use as reagents for heterocyclic synthesis as well as carboxylic acid synthons.[4]

## EXPERIMENTAL SECTION

IR spectra were recorded on Perkin-Elmer 297 or 681 spectrophotometers. $^1H$ NMR spectra were obtained, if not specified, on Varian XL-200 or VXR-200 spectrometers [δ=0 (TMS), $CDCl_3$, J in Hertz]. $^{13}C$ NMR spectra were recorded at 20 MHz on Varian CFT-20 and at 50 MHz on Varian XL-200 or VXR-200 (δ in ppm relative to internal TMS, J in Hertz). $^{15}N$ NMR spectra were recorded at 50 MHz on Brücker AM-500 spectrometer (δ in ppm relative to external nitromethane 80% in $C_6D_6$, J in Hertz, obtained by INEPT sequence). Mass spectra were measured on Varian MAT-44 or Finnigan MAT-TSQ70 spectrometers (electronic impact 70 eV or chemical ionization 100 eV with 200 μBar isobutane as ionizing gas). GLC analysis were performed on CARLO ERBA type chromatograph (detector: FID, nitrogen) equiped with a capillary column (polydimethoxysiloxane RSL-150, 25m long). Most compounds described in this paper could be obtained in a satisfactory state of purity (≥ 95% as ascertained by $^1H$ NMR but no analytically pure samples could be obtained). Distillations were performed using a 10 cm Vigreux column or a Büchi Kugelrohr GKR-50 apparatus. All dry solvents were distilled under argon or in vacuo. Tetrahydrofurane (THF) and ether ($Et_2O$) were distilled from sodium-benzophenone ketyl. Petroleum ether, dichloromethane, acetonitrile, triethylamine (TEA), diisopropylamine, formamide, trimethylsilyl chloride (TMS-Cl), t-butyldimethylsilyl chloride (TBDMS-Cl) and thexyldimethylsilyl chloride (THDMS-Cl, gift from Ciba-Geigy, Basel) and isopropanol were distilled from calcium hydride. Methanol and ethanol were distilled from their respective magnesium alkoxides. Acid chlorides and aldehydes were distilled immediately before use. All reactions requiring anhydrous or inert conditions were run under a positive pressure of argon.

Trimethylsilyl triflate,[15] t-butyldimethylsilyl triflate,[16] isopropyl formimidate hydrochloride,[6] acetimidate,[5] benzimidate,[5] lithium hexamethyldisilazanate,[17] t-butylhypochlorite,[18] di-t-butyltetramethyldisilazane,[19] N-trialkylsilylimines[8,9] and non commercial acid chlorides[20] have been prepared according to the procedures reported in the literature.

SYNTHESIS OF N-ACYLIMIDATES:

### *General procedure*

To a vigorously stirred solution of isopropyl formimidate hydrochloride in dry dichloromethane (0.5 M) at -35°C, was added at once triethylamine and then the acid chloride. Petroleum ether was then added in one portion to the reaction mixture and the cooling bath was removed. The mixture was filtered and the filtrate was concentrated under vacuum. The residue was again dissolved in petroleum ether and any insoluble material removed by filtration. The solution was concentrated and the resulting oil purified by distillation.

### N-acetyl isopropyl formimidate 3a

20 g (162 mmols) of isopropyl formimidate hydrochloride, 350 ml of $CH_2Cl_2$, 47 ml (356 mmols) of $Et_3N$, 11.5 ml (162 mmols) of acetyl chloride; yield: 15.7 g (76%); bp: 55°C/12mm Hg. $^1H$ NMR: 8.02 (br s, 1H); 5.10 (septxd, 1H, $^3J$=6.2, $^4J$=0.8); 2.22 (s, 3H); 1.31 (d, 6H). $^{13}C$ NMR: 183.13 (sxm); 159.27 (dxd, $^1J$=201.3, $^3J$=3.0); 70.97 (dxsept, $^1J$=149.2, $^2J$=4.2); 26.17 (q, $^1J$=127.9); 21.39 (qxm, $^1J$=122.0). IR (neat): 2980; 2940; 2880; 1700; 1600; 1375; 1190; 1105; 990; 900; 770; 730; 675.

### N-propionyl isopropyl formimidate 3b

21.8 g (176 mmols) of isopropyl formimidate hydrochloride, 53.9 ml (387 mmols) of $Et_3N$, 15.29 ml (176 mmols) of propionyl chloride; yield: 17.64 g (70%); bp: 60°C/12mm Hg. $^1H$ NMR: 8.01 (br s, 1H); 5.09 (septxd, 1H, $^3J$=6.2, $^4J$=0.9); 2.50 (q, 2H, $^3J$=7.4); 1.31 (d, 6H); 1.13 (t, 3H). $^{13}C$ NMR ($C_6D_6$): 186.38 (sxm); 159.29 (dxd, $^1J$=201.2, $^3J$=3.0); 70.89 (dxsept, $^1J$=153.2, $^2J$=4.5); 32.53 (txq, $^1J$=125.9, $^2J$=3.9);

21.40 (qxm, $^1J$=125.0); 8.80 (qxt, $^1J$=127.4, $^2J$=3.4). IR (neat): 2980; 2940; 2880; 1700; 1610; 1460; 1375; 1280; 1185; 1140; 1110; 1070; 910; 810; 785.

**N-hexanoyl isopropyl formimidate 3c**

9.73 g (79 mmols) of isopropyl formimidate hydrochloride, 25.0 ml (174 mmols) of $Et_3N$, 11.05 ml (79 mmols) of hexanoyl chloride; yield: 9.73 g (66%); bp: 90°C/0.5mm Hg. $^1H$ NMR: 8.01 (br s, 1H); 5.01 (septxd, 1H, $^3J$=6.3, $^4J$=0.6); 2.43 (t, 2H, $^3J$=7.5); 1.70 and 1.20 (m, 2H+4H); 1.10 (d, 6H); 0.89 (m, 3H). $^{13}C$ NMR ($C_6D_6$): 186.29 (sxm); 160.04 (dxd, $^1J$=200.7, $^3J$=3.2); 71.31 (dxm, $^1J$=144.9, $^2J$=4.3); 40.04 (txt, $^1J$=125.9, $^2J$=3.8); 32.22 (txm, $^1J$=125.0); 25.19 (txm, $^1J$=125.0); 23.30 (txm, $^3J$=125); 21.89 (qxm, $^1J$=126.6); 14.60 (qxm, $^1J$=123.7). IR (neat): 3000-2900; 2865; 1700; 1610; 1470; 1380; 1280; 1250; 1150; 1120; 920; 800.

**N-phenylacetyl isopropyl formimidate 3d**

4 g (32.4 mmols) of isopropyl formimidate hydrochloride, 5.9 g (32.4 mmols) of phenylacetyl chloride, 9.9 ml (71.3 mmols) of $Et_3N$; yield: 4.9 g (75%); bp: 85°C/0.02mm Hg. $^1H$ NMR: 7.92 (s, 1H); 7.32-7.23 (m, 5H); 5.05 (sept, 1H, $^3J$=6.25); 3.76 (s, 2H); 1.26 (d, 6H, $^3J$=6.23). $^{13}C$ NMR: 184.43 (sxm); 159.49 (d, $^1J$=201.0); 134.41 (sxm); 129.48 (dxm, $^1J$=157.9); 128.37 (dxm, $^1J$=166.4); 126.77 (dxm, $^1J$=160.4); 71.53 (dxm, $^1J$=149.0); 46.31 (txm, $^1J$=128.6); 21.39 (qxm, $^1J$=130.2). IR (neat): 3060; 3040; 2900; 1700; 1610; 1370; 1200; 1130.

**N-hydrocinnamoyl isopropyl formimidate 3e**

4 g (32.4 mmols) of isopropyl formimidate hydrochloride, 4.8 ml (32.4 mmols) of hydrocinnamoyl chloride, 9.9 ml (71.3 mmols) of $Et_3N$; yield: 5.2g (73%); bp: 165°C/0.03mm Hg. $^1H$ NMR: 7.97 (s, 1H); 7.32-7.18 (m, 5H); 5.08 (sept, 1H, $^3J$=6.3); 3.01-2.93 (m, 2H); 2.85-2.70 (m, 2H); 1.30 (d, 6H). $^{13}C$ NMR: 186.24 (sxm); 159.55 (d, $^1J$=200.1); 140.85 (sxm); 128.38 (dxm, $^1J$=159.1); 128.24 (dxm, $^1J$=162.2); 126.03 (dxm, $^1J$=157.3); 71.52 (dxm, $^1J$=149.1); 40.78 (txm, $^1J$=128.2); 30.68 (txm, $^1J$=130.0); 21.44 (qxm, $^1J$=125.7). IR (neat): 3060; 3040; 2900; 1700; 1610; 1380; 1200; 1130.

**N-(3,3-dimethylbutanoyl) isopropyl formimidate 3f**

1.53 g (12.4 mmols) of isopropyl formimidate hydrochloride, 1.67 g (12.4 mmols) of 3,3-dimethyl propionyl chloride, 3.63 ml (26 mmols) of $Et_3N$; yield: 1.63 g (72%); bp: 150°C/0.05mm Hg. $^1H$ NMR: 8.00 (s, 1H); 5.09 (sept, 1H, $^3J$=6.2); 2.38 (s, 2H); 1.33 (d, 6H, $^3J$=6.2); 1.07 (s, 9H). $^{13}C$ NMR: 185.91 (sxm); 158.72 (d, $^1J$=149.2); 77.21 (dxm, $^1J$=128.3); 52.49 (txm, $^1J$=126.4); 29.70 (q, $^1J$=126.1); 21.39 (qxm). IR (neat): 2900; 1700; 1610; 1470; 1390; 1210; 1135; 1100.

**N-vinylacetyl isopropyl formimidate 3g**

1 g (8 mmols) of isopropyl formimidate hydrochloride, 0.84 g (8 mmols) of vinylacetyl chloride, 1.62 g (16 mmols) of $Et_3N$; temperature:-78°C; yield: 0.65 g (52%); bp: 80°C/1mm Hg. $^1H$ NMR: 8.02 (s, 1H); 6.01 (m, 1H); 5.19 (m, 2H); 5.13 (sept, 1H, $^3J$=6.2); 3.28 (d, 2H, $^3J$=6.8); 1.34 (d, 6H, $^3J$=6.2). IR (neat): 1700, 1610.

**N-fluoroacetyl isopropyl formimidate 3h**

11.1 g (90 mmols) of isopropyl formimidate hydrochloride, 27.6 ml (198 mmols) of $Et_3N$, 8.7 g (90 mmols) of fluoroacetyl chloride; yield: 9.72 g (73%); bp: 45-48°C/0.3mm Hg. $^1H$ NMR: 8.32 (br s, 1H); 5.20 (sept, 1H, $^3J$=6.2); 5.00 (d, 2H, $^2J$=47.4); 1.36 (d, 6H). $^{13}C$ NMR: 180.21 (sxm); 162.21 (dxdxd, $^4J$=4.3, $^1J$=202.2, $^3J$=4.0); 80.99 (dxt, $^1J$=181.4, $^1J$=153.0); 72.08 (dxm, $^1J$=149.6, $^2J$=4.5); 20.70 (qxm, $^1J$=127.0). IR (neat): 3000; 2860; 1700; 1600; 1510; 1385; 1290; 1155; 1100; 1050; 900; 790.

**N-chloroacetyl isopropyl formimidate 3i**

11.88 g (96 mmols) of isopropyl formimidate hydrochloride, 30.8 ml (221 mmols) of $Et_3N$, 7.7 ml (96 mmols) of chloroacetyl chloride; yield: 9.89 g (60%); bp: 50°C/0.3mm Hg. $^1H$ NMR: 8.22 (br s, 1H); 5.17 (septxd, 1H, $^3J$=6.2, $^4J$=0.9); 4.26 (s, 2H); 1.35 (d, 6H). $^{13}C$ NMR: 178.06 (sxm); 160.91 (dxd, $^1J$=202.6, $^3J$=3.5); 71.50

(dxm, $^1J$=150.0); 44.76 (t, $^1J$=150.8); 20.35 (qxm, $^1J$=127.0). IR (neat): 2985, 2880, 1715, 1600, 1470, 1375, 1315, 1270, 1210, 1130, 1100, 900, 795, 730.

**N-isobutyryl isopropyl formimidate 3j**

11.4 g (92.3 mmols) of isopropyl formimidate hydrochloride, 28.3 ml (203 mmols) of $Et_3N$, 9.6 ml (92.3 mmols) of isobutyryl chloride; yield: 9.22 g (63%); bp: 67-70°C/12mm Hg. $^1H$ NMR: 7.99 (br s, 1H); 5.10 (sept, 1H, $^3J$=6.2); 2.65 (sept, 1H, $^3J$=7.0); 1.32 (d, 6H); 1.17 (d, 6H). $^{13}C$ NMR ($C_6D_6$): 189.07 (sxm); 159.78 (dxd, $^1J$=201.1, $^3J$=3.3); 70.91 (dxsept, $^1J$=152.3, $^2J$=4.3); 38.01 (dxsept, $^1J$=127.2, $^2J$=4.0); 21.45 (qxm, $^1J$=132.2); 18.81 (qxm, $^1J$=127.0). IR (neat): 2980 ; 2940; 2880; 1700; 1610; 1470; 1390; 1280; 1180; 930.

**N-acetyl ethyl acetimidate 3m**

15 g (126 mmols) of ethyl acetimidate hydrochloride, 38.7 ml (278 mmols) of $Et_3N$, 8.9 ml (126 mmols) of acetyl chloride; room temperature; yield: 14.1 g (83%); bp: 57°C/10mm Hg. $^1H$ NMR: 4.09 (q, 2H, $^3J$=7.1); 2.17 (s, 3H); 2.02 (s, 3H); 1.28 (t, 3H). $^{13}C$ NMR ($C_6D_6$): 182.46 (q, $^2J$=6.8); 160.98 (sxm); 62.38 (txq, $^1J$=146.9, $^2J$=4.5); 25.87 (q, $^1J$=127.7); 17.18 (q, $^1J$=128.5); 13.76 (qxt, $^1J$=126.9, $^2J$=2.1). IR (neat): 2980; 1700; 1670; 1380; 1305; 1235; 1060; 1040; 965; 870; 775.

**N-propionyl ethyl acetimidate 3n**

13.8 g (112 mmols) of ethyl acetimidate hydrochloride, 34.2 ml (246 mmols) of $Et_3N$, 9.7 ml (112 mmols) of propionyl chloride; room temperature; yield: 13.9 g (87%); bp: 75°C/10mm Hg. $^1H$ NMR: 4.10 (q, 2H, $^3J$=7.1); 2.42 (q, 2H, $^3J$=7.5); 2.00 (s, 3H); 1.28 (t, 3H); 1.13 (t, 3H). $^{13}C$ NMR ($C_6D_6$): 185.66 (sxm); 161.33 (sxm); 62.42 (txq, $^1J$=147.3, $^2J$=4.6); 32.30 (txq, $^1J$=126.1, $^2J$=4.0); 17.35 (q, $^1J$=129.8); 13.87 (qxt, $^1J$=126.8, $^2J$=2.5); 8.76 (qxt, $^1J$=126.9, $^2J$=3.9). IR (neat): 2980; 1700; 1665; 1380; 1290, 1195; 1160; 1055; 935; 870.

**N-acetyl methyl benzimidate 3o**

20.94 g (122 mmols) of methylbenzimidate hydrochloride, 37.3 ml (268 mmols) of $Et_3N$, 8.67 ml (122 mmols) of acetyl chloride; room temperature; yield: 15.5 g (72%); bp: 63°C/0.2mm Hg. $^1H$ NMR: 7.70-7.40 (m, 5H); 3.90 (s, 3H); 2.20 (s, 3H). $^{13}C$ NMR: 182.30; 157.15; 132.40; 131.53; 126.40; 156.05; 55.19; 26.98. IR (neat): 3100; 2950; 1730-1620; 1440; 1360; 1320; 1280; 1180; 1120; 1000; 960; 920; 780; 700; 640.

SYNTHESIS OF 2-AZADIENES **4**

*Method A : **General procedure***

To a solution of N-acylimidate (0.5 M) and triethylamine in dry ether was added dropwise the trialkylsilyl triflate diluted in ether. Two phases were observed. The upper ethereal phase was removed and the lower phase washed twice with two portions of ether. The combined ethereal fractions were concentrated in vacuo and the residue was purified by distillation.

*Method B : **General procedure***

To a solution of compound **6** in dry ether (1 M), was added at once the triethylamine. To this mixture, was added dropwise the acid chloride diluted in dry ether. Stirring was maintained for two hours at room temperature. The precipitate (triethylamine hydrochloride) was filtered on celite and washed with two portions of ether. The filtrate was concentrated under reduced pressure and the resulting crude product was purified by bulb-to-bulb distillation under vacuum.

**N-t-butyldimethylsilyl isopropyl formimidate 6**

A solution of 10 g (81 mmols) of isopropyl formimidate chloride and 100 ml of dry $CH_2Cl_2$ was cooled at -40°C. At this temperature, 24.8 ml (178 mmols) of triethylamine was added at once and then dropwise a solution of 18.6 ml (81 mmols) of t-butyldimethylsilyl triflate in 50 ml of dichloromethane. During the addition, the temperature should be maintained at -40°C. After complete addition of the t-butyldimethylsilyl triflate, 200 ml of petroleum ether was added at once and the cooling bath was removed. When the mixture has reached room temperature, the precipitate was filtered on celite and rinced three times with three portions of petroleum ether.

The solvants were removed under reduced pressure. After addition of dry ether, the residual triethylammonium triflate was removed by decantation. The ethereal solution was evaporated under vacuum. The residue contained compound **6** (purity ≥ 95%) which was too unstable to be easily purified. It can however be easily kept at -20°C without decomposition. It was used as such in the acylation step. Yield: 14.7 g crude (90%); colourless oil; bp: 62-65°C/12mm Hg. $^1$H NMR: 7.64 (s, 1H); 5.08 (sept, 1H, $^3$J=6.3); 1.25 (d, 6H, $^3$J=6.3); 0.90 (s, 9H); 0.09 (s, 6H). $^{13}$C NMR: 154.04; 65.70; 25.89; 21.84; 17.19; -5.33. IR (neat): 2960; 2940; 2860; 1670; 1470; 1375; 1255; 1185; 1175; 1110; 915; 840; 770. MS (EI, $C_{10}H_{23}NOSi$): m/z= 201 ($M^{+\cdot}$, 8%); 173 (1%) ; 160 (6%) ; 144 (22%); 117 (100%) ; 102 (42%); 75 (38%); 59 (20%); 57 (6%) ; 43 (17%).

**1-isopropoxy-3-t-butyldimethylsilyloxy-2-aza-1,3-butadiene 4a**

*method A:* 3.5 g (27 mmols) of N-acetyl isopropyl formimidate, 4.2 ml (30 mmols) of $Et_3N$, 7.19 g (27 mmols) of t-butyldimethylsilyl triflate; yield: 5.05 g (77%).

*method B:* 4 g (20 mmols) of N-t-butyldimethylsilyl isopropyl formimidate, 2.77 ml (20 mmols) of $Et_3N$, 1.42 ml (20 mmols) of acetyl chloride; yield: 3.6 g (74%); colourless oil; bp: 90°C/0.03mm Hg. $^1$H NMR: 7.91 (s, 1H); 5.08 (sept, 1H, $^3$J=6.2); 4.00 (s, 1H); 3.79 (s, 1H); 1.29 (d, 6H, $^3$J=6.2); 0.95 (s, 9H); 0.20 (s, 6H). $^{13}$C NMR: 155.18 (dxdxd, $^2$J=1.6, $^3$J=5.9); 154.73 (dxdxd, $^1$J=198.7, $^3$J=3.2, $^4$J=1.3); 82.71 (dxd, $^1$J=159.7, $^1$J=161.5); 69.24 (dxm, $^1$J=150.4); 25.63 (qxm, $^1$J=125.3); 21.69 (qxm, $^1$J=126.4); 18.11 (sxm); -4.83 (qxm, $^1$J=118.2). $^{15}$N NMR: -131.10 (dxdxdxd, $^2$J=2.2, $^3$J=5.8, $^3$J=2.2, $^4$J=0.7). IR (neat): 3000-2850; 1630; 1470; 1370; 1260; 1220; 1200; 1110; 1070; 1020; 920; 830; 785.

**1-isopropoxy-3-t-butyldimethylsilyloxy-2-aza-1,3-pentadiene 4b**

*method A:* 2.0 g (14 mmols) of N-propionyl isopropyl formimidate, 1.5 g (15 mmols) of $Et_3N$, 3.69 g (14 mmols) of t-butyldimethylsilyl triflate; yield: 2.66 g (74%).

*method B:* 4 g (20 mmols) of t-butyldimethylsilyl isopropyl formimidate, 13.8 ml (99.5 mmols) of $Et_3N$, 1.73 ml (20 mmols) of propionyl chloride; yield: 3.94 g (77%); colourless oil; bp: 100°C/0.03mm Hg. $^1$H NMR: 7.69 (s, 1H); 5.03 (sept, 1H, $^3$J=6.2); 4.18 (q, 1H, $^3$J=6.8); 1.59 (d, 3H, $^3$J=6.8); 1.29 (d, 6H, $^3$J=6.2); 0.95 (s, 9H); 0.15 (s, 6H). $^{13}$C NMR: 153.21 (dxm, $^1$J=197.5, $^3$J=3.2); 151.27 (sxm); 88.94 (dxq, $^1$J=156.4, $^2$J=7.1); 69.05 (dxsept, $^1$J=147.7, $^2$J=4.4); 25.77 (qxm, $^1$J=125.3); 21.77 (qxm, $^1$J=127.6); 18.15 (sxm); 10.71 (qxd, $^1$J=126.4, $^2$J=2.7); -3.84 (qxm, $^1$J=119.1). $^{15}$N NMR : -185.90 (m). IR (neat): 3000-2850; 1660; 1635; 1465; 1380; 1325; 1250; 1190; 1180; 1110; 1065; 925; 840; 780. MS (EI, $C_{13}H_{27}NO_2Si$): m/z= 257 ($M^{+\cdot}$, 10%); 214 (18%); 200 (55%); 186 (5%); 158 (78%); 102 (70%); 100 (10%) ; 75 (100%) ; 73 (80%) ; 59 (17%) ; 57 (22%) ; 43 (25%).

**1-isopropoxy-3-t-butyldimethylsilyloxy-2-aza-1,3-octadiene 4c**

*method A:* 2.4 g (14.2 mmols) of N-hexanoyl isopropyl formimidate, 2.38 ml (17.1 mmols) of $Et_3N$, 3.27 ml (14.2 mmols) of t-butyldimethylsilyl triflate; yield: 2.58 g (64%); bp: 120°C/0.03mm Hg. $^1$H NMR: 7.68 (s, 1H); 5.06 (sept, 1H, $^3$J=6.2); 4.16 (q, 1H, $^3$J=7.1); 2.24 (m, 2H); 1.40 (m, 4H); 1.11 (d, 6H, $^3$J=6.2); 1.06 (s, 9H); 0.94 (m, 3H); 0.27 (s, 6H). $^{13}$C NMR: 153.88 (dxm, $^1$J=191.3, $^3$J=2.8); 152.31 (sxm, $^2$J=2.9, $^3$J=5.6); 94.21 (dxm, $^1$J=154.0); 69.53 (dxm, $^1$J=150.0); 33.40 (txm, $^1$J=128.0); 26.57 (qxm, $^1$J=125.0); 26.10 (txm, $^1$J=130.0); 23.29 (txm, $^1$J=130.0); 22.33 (qxm, $^1$J=130.0); 18.92 (sxm), 14.78 (qxm, $^1$J=124.0); -2.98 (qxm, $^1$J=118.0). IR (neat): 2980-2860; 1635; 1465; 1365; 1255; 1210; 1170; 1110; 1080; 1000; 910; 840; 780. MS (EI, $C_{16}H_{33}NO_2Si$) : m/z= 299 ($M^{+\cdot}$, 40%); 256 (90%); 242 (80%); 214 (85%); 200 (100%); 172 (60%); 130 (40%); 102 (82%); 75 (95%); 73 (95%); 59 (30%); 43 (50%).

**1-isopropoxy-4-phenyl-3-t-butyldimethylsilyloxy-2-aza-1,3-butadiene 4d**

*method A:* 1.674 g (8 mmols) of N-phenylacetyl isopropyl formimidate, 1.14 ml (8 mmols) of $Et_3N$, 2.15 g (8 mmols) of t-butyldimethylsilyl triflate; yield: 2.13 g (82%).

*method B:* 4 g (20 mmols) of N-t-butyldimethylsilyl isopropyl formimidate, 2.77 ml (20 mmols) of $Et_3N$, 2.62 ml (20 mmols) of phenylacetyl chloride; yield: 4.82 g (76%); pale yellow oil; bp: 150°C/0.03mm Hg. $^1$H NMR: 7.86 (s, 1H); 7.53 (m, 2H); 7.25 (m, 3H); 5.12 (sept, 1H, $^3$J=6.2); 5.05 (s, 1H); 1.35 (d, 3H, $^3$J=6.2); 1.01(s, 9H); 0.22 (s, 6H). $^{13}$C NMR: 154.59 (dxd, $^1$J=198.7, $^3$J=3.2); 153.44 (dxd, $^2$J=2.0, $^3$J=5.5); 137.53 (txd, $^2$J=1.2, $^3$J=7.6); 128.30 (dxd, $^1$J=159.2, $^3$J=7.9); 127.88 (dxq, $^1$J=158.9, $^3$J=6.7); 124.93 (dxd, $^1$J=160.0, $^3$J=7.3); 94.10 (dxt, $^1$J=153.8, $^3$J=4.5); 70.26 (dxsept, $^1$J=148.0, $^2$J=4.3); 26.37 (qxm, $^1$J=125.2); 22.25

(qxm, $^1J$=126.6); 18.63 (sxm); -2.91 (qxm, $^1J$=119.4). $^{15}N$ NMR: -130.45 (m, $^2J$=1.8). IR (neat): 3060; 3020; 2960; 1635; 1600; 1575; 1450; 1375; 1260; 1170; 1110; 1020; 910; 840, 810. MS (EI, $C_{18}H_{29}NO_2Si$): m/z= 319 ($M^{+\cdot}$, 9%), 262 (4%); 220 (10%); 202 (10%); 193 (29%); 179 (26%); 117 (18%) ; 91 (28%); 75 (100%); 73 (25%); 57 (20%); 43 (39%).

**1-isopropoxy-5-phenyl-3-t-butyldimethylsilyloxy-2-aza-1,3-pentadiene 4e**

*method A:* 1.64 g (7.5 mmols) of N-hydrocinnamoyl isopropyl formimidate, 1.04 ml (7.5 mmols) of $Et_3N$, 1.72 ml (7.5 mmols) of t-butyldimethylsilyl triflate; yield: 1.91 g (81%).

*method B:* 4 g (20 mmols) of N-t-butyldimethylsilyl isopropyl formimidate, 13.9 ml (100 mmols) of $Et_3N$, 2.96 ml (20 mmols) of hydrocinnamoyl chloride; yield: 4.84 g (73%); colourless oil; bp: 150°C/0.03mm Hg. $^1H$ NMR: 7.73 (s, 1H); 7.25 (m, 5H); 5.03 (sept, 1H, $^3J$=6.2); 4.24 (t, 1H, $^3J$=7.3); 3.40 (d, 2H, $^3J$=7.3); 1.27 (d, 6H, $^3J$=6.2); 0.98 (s, 9H); 0.20 (s, 6H). $^{13}C$ NMR: 153.74 (dxm, $^1J$=196.7); 151.90 (sxm); 142.43 (sxm); 128.22 (dxm, $^1J$=158.8); 128.14 (dxm, $^1J$=159.1); 125.48 (dxm, $^1J$=157.3); 92.10 (dxt, $^1J$=157.6, $^2J$=6.8); 69.29 (dxsept, $^1J$=147.9, $^2J$=4.3); 31.73 (txm, $^1J$=126.9); 25.80 (qxm, $^1J$=125.2); 21.78 (qxm, $^1J$=126.3); 18.11 (sxm); -3.69 (qxm, $^1J$=119.0). $^{15}N$ NMR: -131.89 (m, $^2J$=1.8, $^3J$=0.7, $^4J$=0.7). IR (neat): 3060; 3030; 2960; 1635; 1600; 1495; 1365; 1255; 1205; 1110; 1030; 910; 840; 785. MS (EI, $C_{19}H_{31}NO_2Si$): m/z= 333 ($M^{+\cdot}$, 3%); 276 (2%) ; 260 (3%) ; 207 (45%); 179 (13%); 132 (7%); 117 (19%); 104 (29%) ; 103 (25%); 91 (19%); 77 (19%); 75 (100%); 73 (18%); 72 (13%); 43 (6%).

**5,5-dimethyl-1-isopropoxy-3-t-butyldimethylsilyloxy-2-aza-1,3-hexadiene 4f**

*method A:* 0.9 g (4.96 mmols) of 3,3-dimethylbutanoyl isopropyl formimidate, 1.29 g (4.86 mmols) of N-t-butyldimethylsilyl triflate, 0.68 ml (4.86 mmols) of $Et_3N$ ; yield: 65% (the compound is contaminated with 25% of the starting acylimidate).

*method B:* 3 g (15 mmols) of N-t-butyldimethylsilyl isopropyl formimidate, 20.8 ml (150 mmols) of $Et_3N$, 2 g (15 mmols) of 3,3-dimethyl butanoyl chloride; yield: 3.12 g (70%); colourless oil; bp: 58-60°C/0.01mm Hg. $^1H$ NMR: 7.61 (s, 1H); 5.20 (sept, 1H, $^3J$=6.2); 3.80 (s, 1H); 1.26 (d, 6H, $^3J$=6.2); 1.09 (s, 9H); 0.96 (s, 9H); 0.19 (s, 6H). $^{13}C$ NMR ($C_6D_6$): 153.66 (dxd, $^1J$=198.7, $^3J$=2.7); 152.11 (dxd, $^2J$=3.9, $^3J$=5.2); 100.36 (dxm, $^1J$=152.7); 69.25 (dxsept, $^1J$=147.6, $^2J$=4.4); 31.19 (qxm, $^1J$=128.6); 30.63 (sxm); 26.40 (qxm, $^1J$=119.4); 21.97 (qxm, $^1J$=125.2); 18.51 (sxm); -2.75 (qxm, $^1J$=119.0). IR (neat): 2970-2880; 1640; 1470; 1400; 1380; 1260; 1160; 1120; 1060; 960; 920; 840. MS (EI, $C_{16}H_{33}NO_2Si$): m/z= 299 ($M^{+\cdot}$, 41%); 284 (77%); 256 (14%); 242 (72%); 200 (43%); 160 (46%); 144 (29%); 117 (20%); 102 (32%); 83 (100%) ; 82 (34%); 75 (61%) ; 73 (49%); 72 (28%); 57 (17%); 43 (17%).

**1-isopropoxy-3-t-butyldimethylsilyloxy-2-aza-1,3,5-hexatriene 4g**

*method B:* 4 g (20 mmols) of N-t-butyldimethyl isopropyl formimidate, 2.77 ml (20 mmols) of $Et_3N$, 2.08 g (20 mmols) of vinylacetyl chloride; yield: 4.3 g (80%); yellow oil; bp: 120°C/0.03mm Hg. $^1H$ NMR: 7.78 (s, 1H); 6.59 (dxdxd, 1H, $^3J$=10.8, $^3J$=16.8, $^3J$=10.5); 5.15-4.90 (m, 3H); 4.76 (dxd, $^3J$=10.8, $^4J$=1.2); 1.29 (d, 6H, $^3J$=6.2); 0.96 (s, 9H); 0.17 (s, 6H). $^{13}C$ NMR: 154.06 (dxd, $^1J$=198.4, $^3J$=2.9); 152.39 (dxd, $^2J$=2.5, $^3J$=3.4); 132.32 (dxm , $^1J$=153.3); 110.20 (dxdxd, $^1J$=154.1, $^1J$=159.1, $^3J$=4.7); 97.04 (dxdxdxd, $^1J$=155.6, $^2J$=2.3, $^3J$=8.0, $^3J$=13.3); 69.61 (dxsept, $^1J$=148.1, $^2J$=4.3); 25.70 (qxm, $^1J$=125.2); 21.68 (qxm, $^1J$=126.5); 18.12 (sxm); -3.83 (qxm, $^1J$=119.3). IR (neat): 3090; 2960-2860; 1635; 1595; 1470; 1420; 1370; 1330; 1250; 1200; 1160; 1050; 945; 880; 840; 785. MS (EI, $C_{14}H_{27}NO_2Si$): m/z= 269 ($M^{+\cdot}$, 34%); 254 (3%); 226 (97%); 212 (23%); 170 (39%); 160 (14%); 152 (43%); 147 (11%); 124 (28%); 115 (17%); 102 (34%); 75 (100%); 73 (80%); 43 (20%).

**4-fluoro-1-isopropoxy-3-t-butyldimethylsilyloxy-2-aza-1,3-butadiene 4h**

*method A:* 3.46 g (23.5 mmols) of N-(fluoroacetyl) isopropyl formimidate, 5.39 ml (23.5 mmols) of N-t-butyldimethylsilyl triflate, 3.59 ml (25.8 mmols) of $Et_3N$ ; yield: 4.87 g (79%); this method gives a mixture (70:30) of Z and E isomers.

*method B:* 4 g (20 mmols) of N-t-butyldimethylsilyl isopropyl formimidate, 27.7 ml (200 mmols) of $Et_3N$, 1.92 g (20 mmols) of fluoroacetyl chloride; this reaction gives a mixture 70:30 of the diene and the corresponding acylimidate **3h** which can be separated by distillation; the diene is obtained as a mixture (70:30) of Z and E stereoisomers; yield: 2.85 g (55%) of diene and 0.7 g (24%) of acylimidate; colourless oil; bp: 48-49°C/0.1mm

Hg. $^1$H NMR: Z isomer: 7.90 (s, 1H); 6.56 (d, 1H, $^2$J=79.1); 4.92 (dxsept, 1H, $^3$J=6.2, $^4$J=0.8); 1.26 (d, 6H, $^3$J=6.2); 0.95 (s, 9H); 0.19 (s, 6H). E isomer: 7.86 (s, 1H); 6.38 (d, 1H, $^2$J=78.8); 5.20 (dxsept, 1H, $^3$J=6.2, $^4$J=0.9); 1.29 (d, 6H, $^3$J=6.2); 0.93 (s, 9H); 0.15 (s, 6H). $^{13}$C NMR ($C_6D_6$, Z isomer): 153.75 (dxdxd, $^1$J=199.2, $^3$J=1.9, $^4$J=12.4); 142.00 (sxm, $^2$J=22.7); 131.50 (dxd, $^1$J=241.6, $^1$J=208.5); 69.21 (dxm, $^1$J=150.0); 26.14 (qxm, $^1$J=125.0); 21.99 (qxm, $^1$J=126.0); 18.83 (sxm); -4.16 (q, $^1$J=117.0). IR (neat): 3960; 2860; 1680; 1635; 1475; 1370; 1320; 1260; 1200; 1110; 1020; 910; 845, 790. MS (EI, $C_{12}H_{24}FNO_2Si$): m/z= 261 ($M^{+\cdot}$, 28%); 218 (4%); 204 (71%); 161 (67%); 134 (10%); 117 (12%); 107 (56%); 104 (42%); 79 (43%); 75 (89%); 73 (100%); 68 (55%); 59 (22%); 57 (16%); 43 (55%).

**4-chloro-1-isopropoxy-3-t-butyldimethylsilyloxy-2-aza-1,3-butadiene 4i**

*method A:* 1.68 g (10.3 mmols) of N-(chloroacetyl) isopropyl formimidate, 2.36 ml (10.3 mmols) of N-t-butyldimethylsilyl triflate, 1.86 ml (13.4 mmols) of $Et_3N$ ; this method gives a mixture (85:15) of Z and E isomers; yield: 2.86 g (69%).

*method B:* 4 g (20 mmols) of N-t-butyldimethylsilyl isopropyl formimidate, 2.77 ml (20 mmol) of $Et_3N$, 1.59 ml (20 mmols) of chloroacetyl chloride; yield: 4.03 g (73%); colourless oil; bp: 120°C/0.03mm Hg. $^1$H NMR (Z isomer): 7.76 (s, 1H); 5.05 (sept+s, 2H, $^3$J=6.2); 1.31 (d, 6H, $^3$J=6.2); 1.01 (s, 9H); 0.24 (s, 6H). E isomer: 7.90 (s, 1H); 5.20 (sept, 1H); 5.10 (s, 1H); 1.36 (d, 6H, $^3$J=6.2); 0.97 (s, 9H); 0.21 (s, 6H). $^{13}$C NMR (Z isomer): 154.43 (dxd, $^1$J=198.7, $^3$J=3.1); 152.44 (dxd, $^2$J=10.1, $^3$J=6.1); 86.36 (d, $^1$J=197.0); 70.01 (dxm, $^1$J=151.1); 25.64 (qxm, $^1$J=125.3); 21.66 (qxm, $^1$J=126.6); 18.23 (sxm); -3.91 (qxm, $^1$J=119.5). IR (neat): 2980; 2860; 1630; 1470; 1370; 1320; 1260; 1240; 1180; 1110; 1040; 910; 845; 790. MS (EI, $C_{12}H_{24}ClNO_2Si$): m/z= 278 ($M^{+\cdot}$+1, 41%); 277 ($M^{+\cdot}$, 38%); 220 (81%); 178 (100%); 151 (25%); 142 (23%); 120 (28%); 102 (47%); 93 (41%); 75 (99%); 73 (85%); 59 (23%) ; 57 (19%) ; 43 (67%).

**1-isopropoxy-4-methyl-3-(t-butyldimethylsilyloxy)-2-aza-1,3-pentadiene 4j**

*method A:* 3.07 g (19.5 mmols) of N-isobutyryl isopropyl formimidate, 4.47 ml (19.5 mmols) of N-t-butyldimethylsilyl triflate, 2.98 ml (21.5 mmols) of $Et_3N$; yield: 4.76 g (90%); bp: 53°C/0.1mm Hg. $^1$H NMR: 7.71 (s, 1H); 5.03 (septxd, 1H, $^3$J=6.3, $^4$J=0.8); 1.73 (s, 3H); 1.65 (s, 3H); 1.29 (d, 6H, $^3$J=6.2); 0.97 (s, 9H); 0.11 (s, 6H). $^{13}$C NMR ($C_6D_6$): 152.79 (dxm, $^1$J=199.1, $^3$J=3.0); 142.77 (sxm, $^3$J=6.4); 102.37 (sept, $^2$J=6.0); 68.39 (dxm, $^1$J=153.0); 26.19 (qxm, $^1$J=125.0); 21.99 (qxm, $^1$J=122.0); 18.63 (qxm, $^1$J=125.0); 18.56 (sxm); 18.45 (qxm, $^1$J=125.0); -3.46 (qxm, $^1$J=120.0). $^{15}$N NMR: -132.61 (m, $^2$J=1.5). IR (neat): 3000-2850; 1665; 1635; 1465; 1260; 1230; 1180; 1165; 1130; 1110; 980; 840; 780. MS (EI, $C_{14}H_{29}NO_2Si$): m/z= 271 ($M^{+\cdot}$, 35%); 228 (20%); 214 (39%); 172 (69%); 102 (80%); 75 (100%); 73 (90%); 59 (20%); 43 (30%).

**4-carbomethoxy-1-isopropoxy-3-t-butyldimethylsilyloxy-2-aza-1,3-butadiene 4k**

*method B:* 4 g (20 mmols) of N-t-butyldimethylsilyl isopropyl formimidate, 2.77 ml (20 mmols) of $Et_3N$, 2.13 ml (20 mmols) of methyl malonyl chloride; yield: 4.25 g (71%) of a mixture (80:20) of Z and E stereoisomers; colourless oil; bp: 120°C/0.03mm Hg. $^1$H NMR (Z isomer): 7.80 (s, 1H); 5.10 (sept, 1H, $^3$J=6.2); 4.59 (s, 1H); 3.67 (s, 3H); 1.34 (d, 6H, $^3$J=6.2); 1.02 (s, 9H); 0.28 (s, 6H). E isomer: 7.80 (s, 1H); 5.25 (sept, 1H, $^3$J=6.2); 4.83 (s, 1H); 3.62 (s, 3H); 1.41 (d, 6H, $^3$J=6.2); 0.96 (s, 9H); 0.25 (s, 6H). $^{13}$C NMR (Z isomer): 166.60 (q, $^3$J=4.0); 164.50 (dxd, $^3$J=3.0, $^3$J=5.5); 155.84 (dxd, $^1$J=199.7, $^3$J=3.2); 83.77 (d, $^1$J=162.0); 70.66 (dxsept, $^1$J=148.4, $^2$J=4.4); 50.01 (qxm, $^1$J=145.5); 25.22 (qxm, $^1$J=125.4); 21.37 (qxm, $^1$J=126.8); 17.93 (sxm); -4.07 (qxm, $^1$J=120.0). IR (neat): 2945-2865; 1725; 1635; 1605; 1470; 1395; 1280; 1265; 1215; 1145; 1110; 1070; 945; 835; 790. MS (EI, $C_{14}H_{27}NO_4Si$): m/z= 301 ($M^{+\cdot}$, 0.4%); 244 (3%); 202 (4%); 175 (64%); 170 (30%); 160 (11%); 144 (7%); 129 (6%); 117 (54%); 101 (48%); 89 (100%); 75 (97%); 73 (10%); 59 (40%); 43 (35%).

**5-(3',4'-dimethoxyphenyl)-1-isopropoxy-3-t-butyldimethylsilyloxy-2-aza-1,3-pentadiene 4l**

*method B:* 2 g (9.95 mmols) of N-t-butyldimethylsilyl isopropyl formimidate, 13.8 ml (99.5 mmols) of $Et_3N$, 2.3 g (10 mmols) of 3-(3',4'-dimethoxyphenyl)-propionyl chloride; yield: 3.43 g crude (83%); this compound is contaminated by 5% of acylimidate; pale yellow oil. $^1$H NMR: 7.73 (s, 1H); 6.77 (m, 3H); 5.04 (sept, 1H, $^3$J=6.2); 4.23 (t, 1H, $^3$J=7.2); 3.87 (s, 3H); 3.85 (s, 3H); 3.34 (d, 2H, $^3$J=7.2); 1.28 (d, 6H, $^3$J=6.2); 0.98 (s, 9H); 0.20 (s, 6H). $^{13}$C NMR ($C_6D_6$): 153.99 (dxd, $^1$J=198.3, $^3$J=2.4); 152.29 (dxdxt, $^2$J=4.4, $^3$J=5.5, $^3$J=5.6); 150.06 (sxm); 148.27 (sxm); 135.44 (sxm); 120.45 (dxm, $^1$J=159.4); 112.96 (dxm, $^1$J=154.6);

112.66 (d, $^1J$=158.0); 92.62 (dxt, $^1J$=157.5, $^2J$=7.2); 69.40 (dxsept, $^1J$=147.6, $^2J$=4.3); 55.61 (q, $^1J$=143.2); 55.56 (q, $^1J$=143.6); 31.84 (txm, $^1J$=126.8); 26.08 (qxm, $^1J$=125.2); 21.84 (qxm, $^1J$=122.6); 18.42 (sxm); -3.37 (qxm, $^1J$=119.1). IR (neat): 2970-2865; 1640; 1600; 1520; 1470; 1370; 1260; 1210; 1160; 1120; 1040; 920; 840; 790. MS (EI, $C_{21}H_{35}NO_4Si$): m/z= 393 ($M^{+\cdot}$, 1.4%); 350 (2%); 336 (1.3%); 188 (30%); 179 (19%); 158 (20%); 151 (60%); 146 (27%); 116 (17%); 102 (24%); 86 (21%); 84 (32%); 75 (100%); 74 (36%); 73 (25%); 59 (8%); 43 (21%).

**4-ethoxy-2-(t-butyldimethylsilyloxy)-3-aza-1,3-pentadiene 4m**

*method A:* 2.22 g (17.2 mmols) of N-acetyl ethyl acetimidate, 3.94 ml (17.2 mmols) of N-t-butyldimethylsilyl triflate, 2.63 ml (18.9 mmols) of $Et_3N$; yield: 3.43 g (82%); bp: 51°C/0.2mm Hg. $^1H$ NMR: 4.06 (q, 2H, $^3J$=7.1); 3.85 (s, 1H); 3.52 (s, 1H); 1.94 (s, 3H); 1.16 (t, 3H); 0.98 (s, 9H); 0.20 (s, 6H). $^{13}C$ NMR ($C_6D_6$): 163.28 (sxm); 157.33 (dxd, $^2J$=2.9); 78.01 (dxd, $^1J$=159.1); 61.49 (txq, $^1J$=146.5, $^2J$=4.5); 25.93 (qxm, $^1J$=125.3, $^3J$=5.3); 18.40 (sxm); 16.07 (q, $^1J$=129.4); 14.26 (qxt, $^1J$=126.2, $^2J$=2.4); -4.16 (q, $^1J$=117.3). IR (neat): 3000-2880; 1680; 1650; 1485; 1390; 1315; 1260; 1070; 1020; 850; 825; 800.

**2-ethoxy-4-t-butyldimethylsilyloxy-3-aza-2,4-hexadiene 4n**

*method A:* 1.61 g (11.2 mmols) of N-propionyl ethyl acetimidate, 2.57 ml (11.2 mmols) of N-t-butyldimethylsilyl triflate, 1.72 ml (12.3 mmols) of $Et_3N$; yield: 2.13 g (74%); bp: 70°C/0.5mm Hg. $^1H$ NMR: 4.12 (q, 2H, $^3J$=7.1); 3.82 (q, 1H, $^3J$=6.6); 2.01 (s, 3H); 1.61 (d, 3H); 1.29 (t, 3H); 0.97 (s, 9H); 0.16 (s, 6H). $^{13}C$ NMR ($C_6D_6$): 163.38 (sxm); 151.40 (sxm); 87.53 (dxq, $^1J$=155.5, $^2J$=6.9); 61.76 (txq, $^1J$=141.9, $^2J$=4.3); 26.69 (qxm, $^1J$=125.0); 19.00 (sxm); 16.65 (q, $^1J$=129.3); 14.98 (qxt, $^1J$=126.3, $^2J$=2.3); 11.17 (qxd, $^1J$=126.0, $^2J$=2.9); -3.01 (q, $^1J$=119.0). IR (neat): 3000-2860; 1660; 1635; 1440; 1350; 1300; 1250; 1200; 1100; 985; 920; 875; 820; 760.

**1-methoxy-1-phenyl-3-(t-butyldimethylsilyloxy)-2-aza-1,3-butadiene 4o**

*method A:* 1.77 g (10 mmols) of N-acetyl methyl benzimidate, 2.3 ml (10 mmols) of N-t-butyldimethylsilyl triflate, 1.53 ml (11 mmols) of $Et_3N$; yield: 2.11 g ( 73%); bp: 120°C/0.5mm Hg. $^1H$ NMR: 7.65 and 7.40 (m, 5H); 3.88 (s, 3H); 3.62 (s, 1H); 3.47 (s, 1H); 0.89 (s, 9H); 0.20 (s, 6H). $^{13}C$ NMR: 155.90; 131.70; 130.29; 128.40; 128.34; 127.90; 78.06; 53.89; 25.58; 18.06; -4.59. IR (neat): 3000-2870; 1700; 1650; 1300; 1200; 1130; 1080; 1030; 850; 790; 710.

SYNTHESIS OF AZADIENES **8**

*method B:* ***General procedure***

To a solution of N-silylated imine in dry ether (1 M), was added at once the triethylamine. To this mixture, was added dropwise the acid chloride in solution in dry ether. Stirring was maintained for two hours at room temperature. The precipitate (triethylamine hydrochloride) was filtered on celite and washed with two portions of ether. The filtrate was concentrated under reduced pressure and the resulting crude product was purified by bulb-to-bulb distillation under vacuum.

*method C:* ***General procedure***

Lithium hexamethyldisilazanate and dry ether (0.5 M) were placed in a 250 ml round bottom flask. After cooling of the mixture at 0°C, a solution of freshly distilled aldehyde in dry ether was added dropwise. After addition of the aldehyde, the reaction was let for one hour at 0°C. Dry triethylamine was then added at once. Afterwards, through the dropping funnel was added dropwise a solution of acid chloride in dry ether. The cooling bath was removed and the reaction was let at room temperature for an extra two hours. The triethylamine hydrochloride was then filtered on celite and the solvent was removed under vacuum. The residue was purified by bulb-to-bulb distillation under vacuum. When the azadiene could not be purified by distillation, the residual lithium trimethylsilanolate was removed by addition of one equivalent of $Me_3SiCl$.

**Dithexyltetramethyldisilazane**

This new compound has been prepared following a general procedure described earlier:[19] 32.6 g (182 mmols) of thexyldimethylsilyl chloride; yield: 22.51 g (82%); colourless liquid; bp: 66-67°C/12mm Hg. $^1$H NMR: 1.64 (sept, 2H, $^3$J=6.9); 0.91 (d, 12H); 0.86 (s, 12H); 0.40 (br.s, 1H); 0.10 (s, 12H). $^{13}$C NMR: 34.30; 24.24; 20.35; 18.62; -1.32. IR (neat): 3470; 3400; 2950; 1550; 1460; 1250; 850. MS (EI, $C_{16}H_{39}NSi_2$): m/z= 302 ($M^{+\cdot}$+1, 34%); 260 (100%); 174 (10%); 147 (88%); 133 (19%); 100 (14%); 84 (20%); 75 (63%); 73 (68%); 49 (15%). GLC (100°C): $R_T$=5.71 min.

**N-thexyldimethylsilyl-2,2-dimethyl propionaldimine 7j**

This new compound has been prepared following a general procedure described in the literature:[8] 20 g (66.3 mmols) of dithexyltetramethyldisilazane, 26.5 ml (66.5 mmols, 2.5 M in hexane) of n-BuLi, 7.2 ml (66.3 mmols) of trimethylacetaldehyde, 8.4 ml (66.2 mmols) of chlorotrimethylsilane; yield: 9 g (60%); colourless liquid; bp: 47-48°C/0.5mm Hg. $^1$H NMR: 8.25 (s, 1H); 1.59 (sept, 1H, $^3$J=6.8); 1.01 (s, 9H); 0.86 (d, 6H, $^3$J=6.8); 0.83 (s, 6H); 0.10 (s, 6H). $^{13}$C NMR: 179.62 (dxm, $^1$J=158.0); 39.24 (sxm); 34.67 (dxm, $^1$J=126.1); 26.05 (qxm, $^1$J=126.0); 24.16 (sxm); 20.62 (qxm, $^1$J=125.1); 18.74 (qxm, $^1$J=124.1); -4.12 (qxm, $^1$J=118.8). IR (neat): 2950; 1690; 1460; 1360; 1250; 840; 820; 775. MS (EI, $C_{13}H_{29}NSi$): m/z= 228 ($M^{+\cdot}$+1, 5%); 158 (100%); 143 (11%); 102 (3%); 100 (3%); 84 (4%); 75 (20%); 73 (9%); 57 (7%) ; 43 (5%).

**N-t-butyldimethylsilyl trifluoroacetaldimine 7v**

*1st step: N-t-butyldimethylsilyl-2,2,2,-trifluoroethylamine*

This new compound has been prepared following a general procedure described earlier:[9] 5 g (50.5 mmols) of 2,2,2-trifluoroethylamine, 7.7 ml (55.5 mmols) of triethylamine, 0.619 g (5.07 mmols) of DMAP, 7.7 g (51.1 mmols) of t-butyldimethylsilyl chloride; time reaction: 3 days; yield: 8.9 g (83%); colourless oil; bp: 70°C/12mm Hg. $^1$H NMR: 3.28 (qxd, 2H, $^3$J=9.2, $^3$J=9.2); 0.92 (s, 9H); 0.05 (s, 6H). $^{13}$C NMR: 125.77 (qxt, $^1$J=278.6, $^2$J=4.7); 45.00 (txqxd, $^1$J=136.4, $^2$J=33.0, $^2$J=2.0); 26.09 (qxm, $^1$J=124.9); 18.20 (sxm); -5.30 (q, $^1$J=118.6). IR (neat): 3430; 2960; 2940; 2860; 1470; 1385; 1280; 1150; 1010; 950; 840; 780; 670. MS (EI, $C_8H_{18}F_3NSi$): m/z =213 ($M^{+\cdot}$, 8%); 156 (49%); 147 (22%); 132 (14%); 106 (38%); 77 (33%); 75 (100%); 73 (6%); 69 (2%); 60 (27%); 57 (20%). HRMS (m/z): calc= 213.1160; found= 213.1155. GLC (80°C): $R_T$=5.08 min.

*2nd step: N-chloro-N-t-butyldimethylsilyl-2,2,2-trifluoroethylamine*

This new compound has been prepared following a general procedure described in the literature:[9] 5 g (23.5 mmols) of N-t-butyldimethylsilyl-2,2,2-trifluoroethylamine, 2.8 g (25.9 mmols) of t-butylhypochlorite; yield: 5.8g crude (100%); bright yellow oil. $^1$H NMR: 3.55 (q, 2H, $^3$J=8.4); 0.90 (s, 9H); 0.12 (s, 6H). $^{13}$C NMR: 124.89 (qxt, $^1$J=281.8, $^2$J=4.0); 56.47 (txq, $^1$J=138.3, $^2$J=32.8); 26.71 (qxm, $^1$J=125.4); 19.89 (sxm); -5.36 (q, $^1$J=120.0). IR (neat): 2960; 2940; 2860; 1475; 1320; 1275; 1190; 1150; 965; 840; 785.

*3rd step: N-t-butyldimethylsilyl trifluoroacetaldimine*

This new compound has been prepared following a general procedure described earlier:[9] 4.5 g (18.2 mmols) of N-chloro-N-t-butyldimethylsilyl-2,2,2-trifluoroethylamine, 2.7 ml (18.1 mmols) of DBU; yield: 3 g (78%); colourless oil; bp: 60°C/12mm Hg. $^1$H NMR: 8.15 (q, 1H, $^3$J=2.9); 0.95 (s, 9H); 0.22 (s, 6H). $^{13}$C NMR: 155.29 (dxq, $^1$J=175.6, $^2$J=39.1); 117.54 (qxd, $^1$J=279.8, $^2$J=22.8); 25.61 (qxm, $^1$J=125.3); 16.87 (sxm); -6.71 (q, $^1$J=119.6). IR (neat): 2960; 2940; 2860; 1725; 1700; 1475; 1365; 1295; 1170; 1010; 945; 840; 780.

**1-phenyl-3-trimethylsilyloxy-2-aza-1,3-butadiene 8a**

*method B:* 4.8 g (27 mmols) of N-trimethylsilylbenzaldimine, 25 ml of $Et_2O$, 4.2 ml (30 mmols) of $Et_3N$, 1.95 ml (27 mmols) of acetyl chloride in 10 ml of $Et_2O$; yield: 4.25 g (72%).

*method C:* 10 g (41 mmols) of LiHMDS, 100 ml of $Et_2O$, 4.2 ml (41 mmols) of benzaldehyde in 10 ml of $Et_2O$, 6.4 ml (45.5 mmols) of $Et_3N$, 2.95 ml (41 mmols) of acetyl chloride in 10 ml of $Et_2O$; yield: 4.53 g (50%); bright yellow oil; bp: 80°C/0.03mm Hg. $^1$H NMR: 8.49 (s,1H); 7.85 (m, 2H); 7.45 (m, 3H); 4.68 (s, 1H); 4.31 (s, 1H); 0.30 (s, 9H). $^{13}$C NMR: 156.59 (dxd, $^3$J=12.2, $^2$J=1.9); 156.28 (dxm, $^1$J=161.9, $^3$J=4.8); 135.75 (sxm); 131.00 (dxt, $^1$J=160.3, $^3$J=7.6); 128.83 (dxm, $^1$J=162.3); 128.47 (dxm, $^1$J=160.2); 91.79 (dxd, $^1$J=158.6, $^1$J=163.4); -0.22 (qxm, $^1$J=119.0). $^{15}$N NMR: -59.48 (dxdxd, $^3$J=6.9, $^3$J=2.5, $^3$J=3.7). IR (neat):

3060; 2960; 1625; 1605; 1590; 1570; 1450; 1350; 1295; 1260; 1220; 1020; 850; 760; 695. MS (EI, $C_{12}H_{17}NOSi$): m/z= 219 ($M^{+\cdot}$, 97%); 218 (100%); 204 (50%); 203 (20%); 202 (70%); 176 (30%); 162 (61%); 135 (40%); 116 (33%); 104 (63%); 103 (38%); 91 (20%); 77 (37%); 75 (60%); 73 (85%).

**1-phenyl-3-trimethylsilyloxy-2-aza-1,3-pentadiene 8b**

*method B:* 5.8 g (33 mmols) of N-trimethylsilylbenzaldimine, 4.54 ml (33 mmols) of $Et_3N$, 2.84 ml (33 mmols) of propionyl chloride; yield: 7.1 g (67%).

*method C:* 10 g (41 mmols) of LiHMDS, 4.2 ml (41 mmols) of benzaldehyde, 6.3 ml (46 mmols) of $Et_3N$, 3.6 ml (41 mmols) of propionyl chloride ; yield: 4.8 g (50%); bright yellow oil; bp: 100°C/0.03mm Hg. $^1H$ NMR: 8.26 (s, 1H); 7.80 (m, 2H); 7.40 (m, 3H); 5.25 (q, 1H, $^3J$=7.3); 1.77 (d, 3H, $^3J$=7.3); 0.27 (s, 9H). $^{13}C$ NMR: 152.70 (dxm, $^1J$=160.0); 152.28 (dxd, $^2J$=2.0, $^3J$=11.7); 136.14 (sxm); 130.46 (dxt, $^1J$=160.5, $^2J$=7.9); 128.47 (dxm, $^1J$=164.0); 128.35 (dxm, $^1J$=164.0); 106.06 (dxq, $^1J$=159.1, $^2J$=8.1); 11.98 (qxd, $^1J$=126.7, $^2J$=2.7); 0.45 (qxm, $^1J$=120.0). $^{15}N$ NMR: -59.96 (m, $^3J$=4.0, $^2J$=2.4). IR (neat): 3060; 3040; 2960; 2900; 1650; 1570; 1450; 1315; 1250; 1180; 1070; 1030; 935; 860; 760. MS (EI, $C_{13}H_{19}NOSi$): m/z= 233 ($M^{+\cdot}$, 100%); 232 (99%); 218 (79%); 216 (60%); 202 (20%); 176 (50%); 162 (75%); 129 (30%); 118 (62%); 104 (30%); 101 (37%); 91 (25%); 77 (20%); 75 (50%); 73 (99%); 59 (65%); 45 (52%).

**1-phenyl-3-trimethylsilyloxy-2-aza-1,3,5-hexatriene 8c**

*method B:* 4.0 g (23 mmols) of N-trimethylsilylbenzaldimine, 3.5 ml (25 mmols) of $Et_3N$, 2.4 g (23 mmols) of vinylacetyl chloride; yield: 3.7 g (67%); yellow-orange oil; bp: 140°C/0.01mm Hg. $^1H$ NMR: 8.41 (s, 1H); 7.80 (m, 2H); 7.40 (m, 3H); 6.66 (dxdxd, 1H, $^3J$=11.2, $^3J$=17.1, $^3J$=10.4); 5.86 (d, 1H, $^3J$=11.2); 5.29 (dxd, 1H, $^2J$=2.0, $^3J$=17.1); 5.09 (dxd, 1H, $^2J$=2.0, $^3J$=10.4); 0.30 (s, 9H). $^{13}C$ NMR: 154.86 (dxm, $^1J$=160.0); 152.20 (sxm, $^3J$=12.6); 135.87 (sxm); 132.11 (dxm, $^1J$=151.9); 130.92 (dxt, $^1J$=160.7, $^3J$=7.6); 128.58 (dxm, $^1J$=158.8); 128.55 (dxm, $^1J$=160.2); 115.57 (txd, $^1J$=156.0, $^3J$=5.2); 111.10 (dxm, $^1J$=156.6); 0.44 (qxm, $^1J$=118.9). IR (neat): 3060; 3040; 2960; 1635; 1610; 1580; 1555; 1450; 1320; 1260; 1140; 850; 760. MS (EI, $C_{14}H_{19}NOSi$): m/z= 245 ($M^{+\cdot}$, 66%); 244 (27%); 230 (12%); 218 (3%); 179 (25%); 147 (34%); 135 (37%); 104 (21%); 103 (11%); 91 (22%); 77 (29%); 75 (100%); 73 (74 %); 59 (23%); 47 (40%); 45 (30%).

**1,4-diphenyl-3-trimethylsilyloxy-2-aza-1,3-butadiene 8d**

*method B:* 1.0 g (5.65 mmols) of N-trimethylsilylbenzaldimine, 0.87 ml (6.24 mmols) of $Et_3N$, 0.75 ml (5.63 mmols) of phenylacetyl chloride; yield: 1.6 g (96%).

*method C:* 5 g (21 mmols) of LiHMDS, 2.1 ml (21 mmols) of benzaldehyde, 3.2 ml (23 mmols) of $Et_3N$, 2.8 ml (20 mmols) of phenylacetyl chloride, 2.7 ml (20 mmols) of trimethylsilyl chloride; yield: 5.8 g (95%) crude compound; yellow-orange oil. $^1H$ NMR: 8.49 (s, 1H); 7.85-7.10 (m, 10H); 5.90 (s, 1H); 0.23 (s, 9H). $^{13}C$ NMR: 155.58; 153.55; 136.36; 135.68; 131.12; 128.68; 128.62; 128.41; 128.01; 125.86; 104.66; 0.66. IR (neat): 3060; 2960; 1630; 1590; 1490; 1450; 1380; 1255; 1140; 1080; 1010; 995; 850; 760. MS (EI, $C_{18}H_{21}NOSi$): m/z= 295 ($M^{+\cdot}$, 8%); 218 (3%); 180 (21%); 165 (89%); 135 (46%); 105 (100%); 91 (52%); 77 (79%); 75 (24%); 73 (32%).

**5,5-dimethyl-1-phenyl-3-trimethylsilyloxy-2-aza-1,3-hexadiene 8e**

*method B:* 4.0 g (23 mmols) of N-trimethylsilyl benzaldimine, 31.4 ml (230 mmols) of $Et_3N$, 3 g (23 mmols) of 3,3-dimethylbutanoyl chloride; yield: 4 g (86%); bright yellow oil; bp: 150°C/0.01mm Hg. $^1H$ NMR: 8.31 (s, 1H); 7.80 (m, 2H); 7.40 (m, 3H); 4.52 (s, 1H); 1.18 (s, 9H); 0.27 (s, 9H). $^{13}C$ NMR: 155.09 (dxt, $^1J$=160.2, $^3J$=4.9); 154.30 (dxd, $^3J$=9.9, $^2J$=2.6); 135.74 (sxm); 130.89 (dxt, $^1H$=160.7, $^3J$=7.6); 128.51 (dxm, $^1J$=159.6); 105.98 (qxm, $^1J$=152.8); 30.55 (sxm); 30.46 (qxm, $^1J$=125.4); 0.97 (qxm, $^1J$=119). IR (neat): 3060; 2960; 1635; 1580; 1450; 1370; 1250; 1150; 1045; 1020; 950; 850; 760; 695. MS(EI, $C_{16}H_{25}NOSi$): m/z= 275 ($M^{+\cdot}$, 26%); 260 (100%); 219 (7%); 218 (7%); 204 (2%); 177 (19%); 162 (16%); 146 (5%); 99 (11%); 91 (12%); 83 (52%); 77 (9%); 75 (21%); 73 (59%); 57 (21%).

**1-phenyl-3-t-butyldimethylsilyloxy-2-aza-1,3-butadiene 8f**

*method B:* 5 g (23 mmols) of N-t-butyldimethylsilyl benzaldimine, 6.4 ml (46 mmols) of $Et_3N$, 1.6 ml (23 mmols) of acetyl chloride; yield: 3.9 g (65%); bright yellow oil; bp: 130°C/0.03mm Hg. $^1H$ NMR: 8.57 (s, 1H);

7.80 (m, 2H); 7.40 (m, 3H); 4.67 (s, 1H); 4.33 (s, 1H); 1.02 (s, 9H); 0.25 (s, 6H). $^{13}C$ NMR: 156.57 (dxd, $^{2}J$=1.6, $^{3}J$=12.2); 156.16 (dxm, $^{1}J$=161.6, $^{3}J$=4.8, $^{4}J$=1.1); 135.77 (sxm); 130.99 (dxt, $^{1}J$=160.3, $^{3}J$=7.6); 128.82 (dxm, $^{1}J$=161.5); 128.49 (dxm, $^{1}J$=161.8); 92.14 (dxd, $^{1}J$=157.9, $^{1}J$=163.1); 25.71 (qxm, $^{1}J$=125.3); 18.29 (sxm); -4.86 (qxm, $^{1}J$=119.2). IR (neat): 3070; 2960; 2860; 1625; 1605; 1595; 1575; 1450; 1365; 1260; 1210; 1015; 940; 845; 810; 695. MS (EI, $C_{15}H_{23}NOSi$): m/z= 261 ($M^{+\cdot}$, 25%); 260 (6%); 246 (5%); 221 (6%); 205 (42%); 204 (60%); 162 (100%); 158 (7%); 147 (4%); 135 (17%); 131 (22%); 130 (15%); 116 (20%); 103 (18%); 93 (17%); 91 (48%); 77 (11%); 75 (37%); 73 (31%); 59 (51%); 57 (7%); 55 (27%).

**1-phenyl-3-t-butyldimethylsilyloxy-2-aza-1,3-pentadiene 8g**

*method B:* 4 g (18 mmols) of N-t-butyldimethylsilyl benzaldimine, 25.5 ml (18 mmols) of $Et_3N$, 1.6 ml (18 mmols) of propionyl chloride; yield: 3.5 g (70%); bright yellow oil; bp: 140°C/0.01mm Hg. $^{1}H$ NMR: 8.35 (s, 1H); 7.75 (m, 2H); 7.40 (m, 3H); 5.09 (q, 1H, $^{3}J$=7.3); 1.73 (d, 3H, $^{3}J$=7.3); 1.01 (s, 9H); 0.15 (s, 6H). $^{13}C$ NMR: 153.46 (dxm, $^{1}J$=160.8, $^{3}J$=4.8); 152.97 (dxdxq, $^{2}J$=2.4, $^{3}J$=6.4, $^{3}J$=11.6); 136.13 (sxm); 130.52 (dxt, $^{1}J$=160.0, $^{3}J$=7.6); 128.48 (dxm, $^{1}J$=156.6); 128.36 (dxm, $^{1}J$=158.6); 102.21 (dxq, $^{1}J$=159.1, $^{2}J$=7.2); 25.83 (qxm, $^{1}J$=125.2); 18.32 (sxm); 11.79 (qxd, $^{1}J$=126.7, $^{2}J$=2.5); -3.78 (qxm, $^{1}J$=119.1). IR (neat): 3060; 2960; 2940; 2860; 1650; 1570; 1450; 1365; 1320; 1260; 1180; 1030; 975; 840; 695.

**5,5-dimethyl-2-trimethylsilyloxy-3-aza-1,3-hexadiene 8h**

*method B:* same procedure with 4 g (26 mmols) of N-trimethylsilyl-2,2-dimethylpropionaldimine, 5.4 ml (38 mmols) of $Et_3N$, 1.85 ml (26 mmols) of acetyl chloride; yield: 3.55 g (70%); bp: 60°C/0.5mm Hg. $^{1}H$ NMR: 7.79 (s, 1H); 4.41 (s, 1H); 4.06 (s, 1H); 1.00 (s, 9H), 0.16 (s, 9H). $^{13}C$ NMR ($C_6D_6$): 168.75 (dxm, $^{1}J$=157.2, $^{4}J$=0.9); 158.30 (dxd, $^{3}J$=12.1, $^{2}J$=2.3); 87.89 (dxd, $^{1}J$=157.7, $^{1}J$=162.4); 36.25 (sxm); 27.04 (qxm, $^{1}J$=128); 0.22 (qxm, $^{1}J$=120). $^{15}N$ NMR: -63.25 (dxdxd, $^{3}J$=6.0, $^{3}J$=2.1, $^{2}J$=4.1). IR (neat): 2960; 2900; 1650; 1630; 1615; 1480; 1460; 1365; 1265; 1210; 1035; 1010; 950; 850; 755.

**2,2-dimethyl-5-trimethylsilyloxy-4-aza-3,5-heptadiene 8i**

*method B:* 4 g (26 mmols) of N-trimethylsilyl-2,2-dimethylpropionaldimine, 17.8 ml (127 mmols) of $Et_3N$, 2.2 ml (26 mmols) of propionyl chloride; yield: 3.6 g (66%); colourless oil; bp: 70°C/0.5mm Hg. $^{1}H$ NMR: 7.63 (s, 1H); 4.86 (q, 1H, $^{3}J$=7.1); 1.64 (d, 3H, $^{3}J$=7.1); 1.07 (s, 9H); 0.20 (s, 9H). $^{13}C$ NMR: 165.75 (dxm, $^{1}J$=152.1); 152.42 (dxdxq, $^{2}J$=2.3, $^{3}J$=11.7, $^{3}J$=6.6); 100.37 (dxq, $^{1}J$=157.7, $^{2}J$=7.1); 35.67 (sxm); 26.69 (qxm, $^{1}J$=126.2); 11.22 (qxd, $^{1}J$=126.6, $^{2}J$=2.7); 0.42 (qxm, $^{1}J$=118.9). IR (neat) : 2960; 1660; 1630; 1480; 1460; 1370; 1330; 1260; 1200; 1180; 1100; 1040; 915; 850; 760. MS (EI, $C_{11}H_{23}NOSi$): m/z= 213 ($M^{+\cdot}$, 26%); 212 (18%); 198 (36%); 184 (12%); 157 (14%); 156 (47%); 142 (13%); 86 (32%); 75 (17%); 73 (100%); 57 (17%); 55 (12%); 45 (17%).

**5,5-dimethyl-2-thexyldimethylsilyloxy-3-aza-1,3-hexadiene 8j**

*method B:* 5 g (22 mmols) of N-thexyldimethylsilyl-2,2-dimethyl propionaldimine, 15.3 ml (110 mmols) of $Et_3N$, 7.8 ml (110 mmols) of acetyl chloride; yield: 3.85 g (65%); colourless oil; bp: 65-67°C/0.05mm Hg. $^{1}H$ NMR: 7.88 (s, 1H); 4.36 (s, 1H); 4.06 (s, 1H); 1.72 (sept, 1H, $^{3}J$=6.9); 1.11 (s, 9H); 0.91 (s, 6H); 0.90 (d, 6H, $^{3}J$=6.9); 0.25 (s, 6H). $^{13}C$ NMR: 169.11 (dxm, $^{1}J$=157.5, $^{4}J$=0.9); 153.13 (dxd, $^{2}J$=2.3, $^{3}J$=12.0); 87.93 (dxd, $^{1}J$=161.9, $^{1}J$=158.0); 35.71 (sxm); 33.81 (dxsept, $^{1}J$=121.3, $^{2}J$=4.2); 26.55 (qxm, $^{1}J$=128.7); 24.67 (sxm); 19.93 (qxm, $^{1}J$=125.3); 18.30 (qxm, $^{1}J$=124.5); -2.95 (qxm, $^{1}J$=119.2). IR (neat): 2960; 2870; 1660; 1635; 1615; 1470; 1370; 1330; 1260; 1150; 1040; 1010; 930; 880; 840; 785. MS (EI, $C_{15}H_{31}NOSi$): m/z= 269 ($M^{+\cdot}$, 1.2%); 185 (58%); 184 (23%); 170 (100%); 157 (14%); 142 (50%); 127 (6%); 116 (9%); 85 (40%); 75 (30%); 73 (32%); 59 (20%); 57 (7%); 43 (20%).

**1-(2-furyl)-3-trimethylsilyloxy-2-aza-1,3-butadiene 8k**

*method B:* 5 g (30 mmols) of N-trimethylsilyl-2-furfuraldimine, 41.7 ml (300 mmols) of $Et_3N$, 2.23 ml (30 mmols) of acetyl chloride; yield: 4.26 g (68%).

*method C:* 10 g (41 mmols) of LiHMDS, 3.4 ml (41 mmols) of 2-furfuraldehyde, 6.3 ml (45 mmols) of $Et_3N$, 3 ml (42 mmols) of acetyl chloride; yield: 4.25 g (50%); bright yellow oil; bp: 48-49°C/0.03mm Hg. $^{1}H$ NMR: 8.30 (s, 1H); 7.60 (d, 1H, $^{3}J$=1.7); 6.90 (d, 1H, $^{3}J$=3.5); 6.57 (dxd, 1H, $^{3}J$=3.5, $^{3}J$=1.7); 4.77 (s, 1H); 4.32

(s, 1H); 0.30 (s, 9H). $^{13}C$ NMR: 156.10 (dxd,$^{3}J$=12.8, $^{2}J$=1.9); 152.34 (sxm); 145.82 (dxdxd, $^{1}J$=203.5, $^{2}J$=10.7, $^{3}J$=7.8); 144.15 (dxd, $^{1}J$=165.2, $^{4}J$=1.2); 116.42 (dxdxd, $^{1}J$=176.7, $^{2}J$=4.5, $^{3}J$=5.0); 112.41 (dxdxd, $^{1}J$=177.5, $^{2}J$=3.1, $^{2}J$=13.3); 93.27 (dxd, $^{1}J$=158.1, $^{1}J$=163.8); 0.00 (qxm, $^{1}J$=119.1). IR (neat): 3130; 2970; 2910; 1630; 1595; 1585; 1570; 1480; 1395; 1260; 1220; 1150; 1020; 935; 850; 750; 695. MS (EI, $C_{10}H_{15}NO_2Si$): m/z= 209 ($M^{+\cdot}$, 100%); 194 (66%); 180 (47%); 167 (12%); 152 (23%); 125 (65%); 94 (36%); 75 (26%); 73 (89%); 45 (27%).

**1-(2-furyl)-3-trimethylsilyloxy-2-aza-1,3-pentadiene 8l**

*method B:* 5 g (30 mmols) of N-trimethylsilyl-2-furfuraldimine, 20.8 ml (150 mmols) of $Et_3N$, 2.6 ml (30 mmols) of propionyl chloride; yield: 4.74 g (71%).

*method C:* 10 g (41 mmols) of LiHMDS, 3.4 ml (41 mmols) of 2-furfuraldehyde, 6.3 ml (45.3 mmols) of $Et_3N$, 3.6 ml (41 mmols) of propionyl chloride; yield: 4.5 g (49%); bright yellow oil; bp: 56-58°C/0.03mm Hg. $^{1}H$ NMR: 8.10 (s, 1H); 7.56 (d, 1H, $^{3}J$=1.8); 6.82 (d, 1H, $^{3}J$=3.5); 6.51 (dxd, 1H, $^{3}J$=3.5, $^{3}J$=1.8); 5.35 (q, 1H, $^{3}J$=7.3); 1.78 (d, 3H, $^{3}J$=7.3); 0.29 (s, 9H). $^{13}C$ NMR: 152.14 (sxm); 151.51 (dxdxq, $^{2}J$=2.3, $^{3}J$=12.6, $^{3}J$=6.9); 144.83 (dxdxm, $^{1}J$=203.5, $^{2}J$=10.7, $^{3}J$=7.8); 140.37 (dxm, $^{1}J$=163.9); 114.52 (dxdxd, $^{1}J$=177, $^{2}J$=3.7, $^{3}J$=5.3); 111.81 (dxdxd, $^{1}J$=176.7, $^{2}J$=3.6, $^{2}J$=13.2); 107.62 (dxq, $^{1}J$=159.4, $^{2}J$=7.5); 12.07 (qxd, $^{1}J$=127.0, $^{2}J$=2.8); 0.25 (qxm, $^{1}J$=119.0). IR (neat): 3120; 2960; 2920; 1650; 1590; 1575; 1480; 1380; 1310; 1260; 1180; 1040; 930; 850; 755. MS (EI, $C_{11}H_{17}NO_2Si$): m/z= 223 ($M^{+\cdot}$, 7%); 208 (3%); 194 (15%); 180 (12%); 169 (22%); 165 (11%); 152 (36%); 147 (5%); 125 (46%); 108 (56%); 94 (8%); 80 (10%); 75 (26%); 73 (100%); 45 (20%).

**1-(2-furyl)-4-phenyl-3-trimethylsilyloxy-2-aza-1,3-butadiene 8m**

*method B:* 2.3 g (14 mmols) of N-trimethylsilyl-2-furfuraldimine, 2.1 ml (15 mmols) of $Et_3N$, 1.82 ml (14 mmols) of phenylacetyl chloride; yield: 3.8 g crude (97%); yellow-orange oil; bp: 125°C/0.03mm Hg. $^{1}H$ NMR: 8.28 (s, 1H); 7.58 (br s, 1H); 7.30 (m, 5H); 6.90 (d, 1H, $^{3}J$=3.5); 6.54 (dxd, 1H, $^{3}J$=3.5, $^{3}J$=1.8); 6.15 (s, 1H); 0.16 (s, 9H). $^{13}C$ NMR: 151.82 (sxm, $^{3}J$=12.0); 149.22 (sxm); 145.16 (dxdxd, $^{1}J$=203.7, $^{2}J$=10.6, $^{3}J$=7.8); 142.34 (d, $^{1}J$=164.2); 135.87 (dxt, $^{2}J$=1.5, $^{3}J$=7.6); 128.32 (dxq, $^{1}J$=159.9, $^{3}J$=6.6); 127.64 (dxd, $^{1}J$=159.8, $^{3}J$=7.7); 125.83 (dxt, $^{1}J$=160.4, $^{3}J$=7.6); 115.18 (dxdxd, $^{1}J$=178.9, $^{2}J$=4.5, $^{2}J$=1.5); 111.90 (dxdxd, $^{1}J$=178.1, $^{2}J$=2.8, $^{2}J$=13.2); 108.62 (dxt, $^{1}J$=157.1, $^{3}J$=4.8); 0.13 (qxm, $^{1}J$=119.2). IR (neat): 3060; 3020; 2960; 1630; 1590; 1580; 1570; 1475; 1445; 1370; 1250; 1140; 1030; 990; 850; 750; 695.

**1-(2-furyl)-3-t-butyldimethylsilyloxy-2-aza-1,3-butadiene 8n**

*method B:* 5 g (24 mmols) of N-t-butyldimethylsilyl-2-furfuraldimine, 16.64 ml (120 mmols) of $Et_3N$, 1.7 ml (24 mmols) of acetyl chloride; yield: 3.84 g (64%); bright yellow oil; bp: 120°C/0.03 mmHg. $^{1}H$ NMR: 8.37 (s, 1H); 7.60 (d, 1H, $^{3}J$=1.8); 6.91 (d, 1H, $^{3}J$=3.5); 6.53 (dxd, 1H, $^{3}J$=3.5, $^{3}J$=1.8); 4.77 (s, 1H); 4.35 (s, 1H); 1.00 (s, 9H); 0.26 (s, 6H). $^{13}C$ NMR: 155.83 (dxd, $^{2}J$=1.7, $^{3}J$=12.6); 152.00 (sxm); 145.51 (dxdxd, $^{1}J$=203.6, $^{2}J$=10.6, $^{3}J$=7.8); 143.68 (dxd, $^{1}J$=165.0, $^{4}J$=1.2); 116.07 (dxdxd, $^{1}J$=176.5, $^{2}J$=4.6, $^{3}J$=5.9); 112.08 (dxdxd, $^{1}J$=177.1, $^{2}J$=3.3, $^{2}J$=13.2); 93.14 (dxd, $^{1}J$=158.0, $^{1}J$=163.9); 25.68 (qxm, $^{1}J$=125.3); 18.27 (sxm); -4.93 (qxm, $^{1}J$=119.3). IR (neat): 3130; 2960; 2900; 1650; 1630; 1585; 1475; 1420; 1390; 1365; 1260; 1210; 1150; 1080; 1020; 965; 885; 840; 785. MS (EI, $C_{13}H_{21}NO_2Si$): m/z= 251 ($M^{+\cdot}$, 1%); 236 (2%); 221 (6%); 195 (32%); 194 (55%); 188 (23%); 169 (60%); 158 (69%); 152 (56%); 125 (89%); 116 (60%); 75 (100%); 73 (57%); 59 (10%); 57 (7%); 43 (29%).

**(Z,E,E)-1,6-diphenyl-2-trimethylsilyloxy-3-aza-1,3,5-hexatriene 8o**

*method B:* 1.55 g (7.64 mmols) of N-trimethylsilyl trans-cinnamaldimine, 1.2 ml (8.63 mmols) of $Et_3N$, 1.01 ml (7.63 mmols) of phenylacetyl chloride; yield: 2.2 g crude (90%).

*method C:* 2.5 g (10 mmols) of LiHMDS, 1.3 ml (10 mmols) of trans-cinnamaldehyde, 1.6 ml (11 mmols) of $Et_3N$, 1.37 ml (10 mmols) of phenylacetyl chloride, 1.3 ml (10 mmols) of trimethylsilyl chloride; yield: 1.7 g crude (51%); red oil. $^{1}H$ NMR: 8.26 (dxd, 1H, $^{3}J$=6.4, $^{4}J$=2.1); 7.60-7.10 (m, 12H); 5.94 (s, 1H); 0.20 (s, 9H). $^{13}C$ NMR: 156.48; 152.60; 143.04; 136.08; 135.33; 129.05; 128.46; 128.41; 127.77; 127.72; 127.07; 125.87; 107.62; 0.35. IR (neat): 3060; 3040; 2960; 1635; 1610; 1580; 1550; 1495; 1450; 1380; 1255; 1140; 1010; 990; 850; 755. MS (EI, $C_{20}H_{23}NOSi$): m/z= 321 ($M^{+\cdot}$, 0.3%); 206 (24%); 191 (11%); 147 (10%); 117 (18%); 91 (8%); 86 (66%); 84 (100%); 75 (29%); 73 (30%); 49 (20%); 47 (29%).

**(E,E)-6-phenyl-2-trimethylsilyloxy-3-aza-1,3,5-hexatriene 8p**

*method C:* 1.3 ml (10 mmols) of trans-cinnamaldehyde, 2.5 g (10 mmols) of LiHMDS, 1.6 ml (10 mmols) of $Et_3N$, 0.74 ml (10 mmols) of acetyl chloride, 1.32 ml (10 mmols) of chlorotrimethylsilane; yield: 0.69 g crude (27%); bright yellow oil. $^1H$ NMR: 8.29 (d, 1H, $^3J$=7.8); 7.55 (m, 2H); 7.40 (m, 3H); 7.27 (d, 1H, $^3J$=15.6); 7.03 (dxd, 1H, $^3J$=7.8, $^3J$=15.6); 4.63 (s, 1H); 4.31 (s, 1H); 0.30 (s, 9H). $^{13}C$ NMR: 157.62; 156.28; 143.75; 135.99; 135.59; 129.20; 128.38; 127.21; 92.23; -0.13.

**(Z,E,E)-1,6-diphenyl-5-methyl-2-trimethylsilyloxy-3-aza-1,3,5-hexatriene 8q**

*method C:* 2.5 g (10 mmols) of LiHMDS, 1.45 ml (10 mmols) of α-methyl-trans-cinnamaldehyde, 1.6 ml (10 mmols) of $Et_3N$, 1.37 ml (10 mmols) of phenylacetyl chloride, 1.32 ml (10 mmols) of chlorotrimethylsilane; in this case, the aldehyde and LiHMDS were allowed to react at room temperature; yield: 2.7 g crude (78%); red oil. $^1H$ NMR: 8.22 (s, 1H); 7.60-7.10 (m, 10H); 6.97 (br s, 1H); 5.71(s, 1H); 2.24 (d, 3H, $^4J$=1.3); 0.22 (s, 9H). $^{13}C$ NMR: 160.75; 154.20; 141.48; 136.86; 136.63; 136.33; 129.42; 129.30; 129.24; 128.22; 127.95; 125.51; 102.09; 12.97; 0.72. IR (neat): 3060; 3040; 2960; 1620; 1580; 1490; 1450; 1380; 1255; 1025; 1010; 910; 850; 755; 700.

**6-methyl-3-trimethylsilyloxy-4-aza-2,4-heptadiene 8r**

*method C* with the following modifications: the aldehyde was added at -30°C. After one hour at -30°C, the reaction's temperature was adjusted at -15°C. The triethylamine was added in once and then, the acid chloride was added dropwise. The cooling bath was removed and the reaction mixture was stirred for two hours at room temperature: 15 g (62 mmols) of LiHMDS, 5.65 ml (62 mmols) of isobutyraldehyde, 9.5 ml (68 mmols) of $Et_3N$, 5.4 ml (62 mmols) of propionyl chloride; yield: 3.7 g (30%); colourless oil; bp: 43-45°C/0.5mm Hg. $^1H$ NMR: 7.61 (d, 1H, $^3J$=5.7); 4.93 (q, 1H, $^3J$=7.1); 2.49 (septxd, 1H, $^3J$=5.7, $^3J$=6.8); 1.65 (d, 3H, $^3J$=7.1); 1.09 (d, 6H, $^3J$=6.8); 0.20 (s, 9H). $^{13}C$ NMR: 163.84 (dxm, $^1J$=156.5); 152.01 (dxdxq, $^2J$=2.4, $^3J$=11.7, $^3J$=6.5); 102.30 (dxq, $^1J$=158.0, $^2J$=7.2); 33.88 (dxm, $^1J$=127.8); 19.40 (qxm, $^1J$=126.6); 11.57 (qxd, $^1J$=126.4, $^2J$=2.7); 0.56 (q, $^1J$=118.7). IR (neat): 2970; 1660; 1630; 1470; 1390; 1315; 1260; 1185; 1040; 930; 850; 765. MS (EI, $C_{10}H_{21}NOSi$): m/z= 199 ($M^{+\cdot}$, 2%); 184 (3%); 156 (27%); 145 (13%); 143 (8%); 128 (22%); 126 (24%); 112 (8%); 100 (42%); 82 (11%); 75 (23%); 73 (100%); 72 (31%); 57 (27%); 55 (22%); 45 (20%); 43 (15%).

**5-methyl-1-phenyl-2-trimethylsilyloxy-3-aza-1,3-hexadiene 8s**

*method C* as for **8s**: 15 g (62 mmols) of LiHMDS, 5.64 ml (62 mmols) of isobutyraldehyde, 9.5 ml (68 mmols) of $Et_3N$, 8.2 ml (62 mmols) of phenylacetyl chloride; yield: 4.1 g (25%); pale yellow oil; bp: 125°C/0.01mm Hg. $^1H$ NMR: 7.84 (d, 1H, $^3J$=4.6); 7.52 (m, 2H); 7.30 (m, 3H); 5.49 (s, 1H); 2.55 (dxsept, 1H, $^3J$=4.6, $^3J$=6.8); 1.15 (d, 6H, $^3J$=6.8); 0.20 (s, 9H). $^{13}C$ NMR: 166.42 (dxm, $^1J$=157.4); 154.14 (dxd, $^2J$=1.9, $^3J$=10.5); 136.31 (txd, $^2J$=1.5, $^3J$=7.7); 127.80 (dxt, $^1J$=159.5, $^3J$=6.8); 127.70 (dxd, $^1J$=160.0, $^3J$=7.5); 125.10 (dxt, $^1J$=160.3, $^3J$=7.6); 99.67 (dxt, $^1J$=155.0, $^3J$=4.7); 33.70 (dxm, $^1J$=127.5); 18.56 (qxm, $^1J$=126.8); 0.51 (qxm, $^1J$=119.1). IR (neat): 3060; 3030; 2960; 2880; 1650; 1630; 1600; 1575; 1495; 1450; 1375; 1255; 1175; 1010; 910; 850; 760; 700. MS (EI, $C_{15}H_{23}NOSi$): m/z= 261 ($M^{+\cdot}$, 7%); 246 (2%); 234 (2%); 218 (1.2%); 172 (7%); 147 (48%); 143 (9%); 127 (10%); 126 (84%); 100 (56%); 86 (10%); 84 (22%); 83 (35%); 75 (38%); 73 (100%); 72 (16%); 57 (12%); 55 (23%); 45 (14%); 43 (18%).

**2-methyl-5-trimethylsilyloxy-4-aza-1,3,5-heptatriene 8t**

*method C:* 15 g (62 mmols) of LiHMDS, 5.15 ml (62 mmols) of methacrolein, 9.5 ml (68 mmols) of $Et_3N$, 5.4 ml (62 mmols) of propionyl chloride; yield: 4.3 g (35%); bright yellow oil; bp: 43-44°C/0.03mm Hg. $^1H$ NMR: 7.98 (s, 1H); 5.62 (s, 1H); 5.44 (s, 1H); 5.10 (q, 1H, $^3J$=7.3); 1.96 (s, 3H); 1.72 (d, 3H, $^3J$=7.3); 0.23 (s, 9H). $^{13}C$ NMR: 156.18 (dxm, $^1J$=161.0); 152.35 (dxdxq, $^2J$=2.1, $^3J$=6.7, $^3J$=12.6); 143.87 (sxm); 124.81 (txm, $^1J$=158.4); 105.13 (dxq, $^1J$=158.4, $^2J$=7.9); 16.78 (qxm, $^1J$=124.1); 11.87 (qxd, $^1J$=129.4, $^2J$=2.8); 0.45 (qxm, $^1J$=118.8). IR (neat): 3080; 2960; 1650; 1580; 1450; 1380; 1310; 1255; 1180; 1040; 845; 760. MS (EI, $C_{10}H_{19}NOSi$): m/z= 197 ($M^{+\cdot}$, 1%); 196 (4%); 182 (3%); 180 (2%); 141 (2%); 126 (13%); 111 (9%); 82 (9%); 75 (21%); 73 (100%); 67 (9%); 59 (14%); 57 (10%); 45 (13%).

SYNTHESIS OF AZADIENES **9**

***General procedure***

A solution of trialkylsilyl triflate (5 M) in dry diethyl ether was added to a mixture of the imide, triethylamine and dry ether. When the addition was complete, stirring was maintained during 30-45 minutes. Two layers appeared and were separated by decantation. The lower layer was washed twice with two portions of ether. The ethereal phases were combined and concentrated under vacuum. The resulting residue was purified by bulb-to-bulb distillation.

**2,6-bis-(trimethylsilyloxy)-3,4-dihydropyridine 9a**

0.565 g (5 mmols) of glutarimide, 2.22 g (10 mmols) of trimethylsilyl triflate, 1.1 g (11 mmols) of triethylamine; yield: 0.625 g (48%); bp: 90°C/0.1mm Hg. $^1$H NMR: 4.23 (m, 1H); 2.12 (m, 4H); 0.20 (s, 9H); 0.13 (s, 9H). IR (neat): 1645; 1610; 1380; 1280; 1240; 1180; 980; 940; 880; 840; 750.

**2,6-bis-(t-butyldimethylsilyloxy)-3,4-dihydropyridine 9b**

0.937 g (8.3 mmols) of glutarimide, 4.38 g (16.6 mmols) of t-butyldimethylsilyl triflate, 1.84 g (18.2 mmols) of triethylamine; yield: 2.9 g (92%); bp:73-75°C/0.05mm Hg. $^1$H NMR: 4.30 (m, 1H); 2.17 (m, 4H); 0.94 (s, 18H); 0.32 (s, 6H); 0.17 (s, 6H). $^{13}$C NMR: 166.40 (sxm); 152.05 (sxm); 84.22 (dxm, $^1$J=159.0); 26.10 (txm); 25.64 (qxm, $^1$J=125.5); 19.77 (txm); 18.02 (sxm); 17.68 (sxm); -4.34 (q, $^1$J=119.0); -4.62 (q, $^1$J=119.0). IR (neat): 1640; 1605; 1380; 1290; 1280; 1240; 1180; 985; 940; 860; 840.

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