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A Protodesilylation Route for 2-Aza-1,3-diene Synthesis

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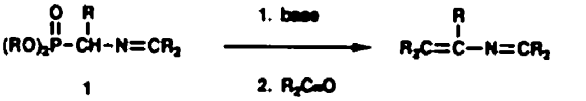
Abstract. A new methodology for 2-aza-1,3-diene synthesis involving protodesilylation reactions of N-1-triethylsilylallyl-imines and their propargyl analogs is described. Synthetic sequences for the preparation of these allyl and propargyl imines starting with propargyl amine are presented. The silylallyl and silylpropargyl imines are transformed to 2-azadiene products by use of CsF induced desilylation via a pathway involving generation and regioselective γ-protonation of intermediate 1-imino-allyl and propargyl anions. Alkylative-desilylation of the silylallyl and propargyl imines leads to generation of N-1-alkylallyl-imines and propargyl analogs via α-alkylation of intermediate anions. Finally, the stereochemistry of azadiene formation has been probed by use of the conversion of N-(1-triethylsilylpropen-1-yl)benzaldimine to 1-phenyl-2-aza-1,3-pentadiene. Solvent, water concentration and a metal cation complexing agent all appear to influence the stereoselectivity of this process.

Substances containing the 2-aza-1,3-diene grouping represent an interesting class of compounds owing to their use as substrates in Diels-Alder cycloaddition processes[1] and as precursors for metalloenamines.[2] In addition, 2-aza-1,3-dienes should be capable of participation in a variety of interesting ground and excited state electrocyclization and 2+2 cycloadditon reactions.[3] The exploration and application of this chemistry is dependent upon the availability of synthetic routes for preparation of these substances. Few general methods have been disclosed thusfar for construction of 2-aza-1,3-dienes.[4] One of these, uncovered by Lavielle[5] and Kaufmann[6] and exploited for synthetic purposes by Martin,[2a] involves Horner-Wadsworth-Emmons chemistry between anions of N-phosphonomethyl imines **1** and ketones or aldehydes (eq. 1). Another general method is modeled after the well-known, base-catalyzed isomerizations of tertiary allylic amines to the corresponding enamines.[7] Worley and Taylor,[8] and Wender and Schaus[9] have independently shown that N-allylimines **2** undergo base-induced, thermodynamically driven isomerization to produce 2-azadienes (eq. 2). The latter methodology is limited by the need to use strongly basic conditions. Thus, it would be difficult to generate 2-azadienes from N-allylimines which possess acidic α-hydrogens. In addition, Wender and Schaus[9] have noted that N-allylimines can also be transformed to 1-azadienes under basic conditions depending upon the substitution pattern present in the allyl-moiety.



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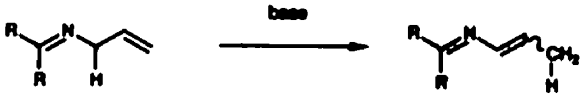

(2)

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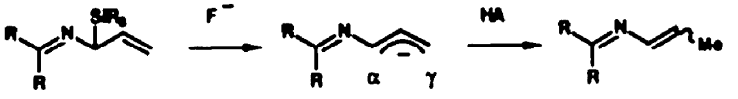
At the outset of our studies in this area, our goal was to find a milder and more selective method for 2-azadiene synthesis. As a result we have explored sequences which are based upon

protodesilylation reactions of allylsilanes. Through the combined efforts of a number of groups, it is known that allylsilanes can be transformed to propene-derivatives via "push" (fluoride ion induced) or "pull" (protic acids) type mechanistic pathways.[10] We anticipated that N-1-(trialkylsilylallyl) imines **3** would behave in a similar manner, and as a result, would undergo fluoride induced protodesilylation to form 2-aza-1,3-dienes (eq. 3). The N-imino-allyl anion intermediates **4** in this scheme were expected to undergo kinetic protonation at the γ-carbon thus furnishing 2-aza-1,3-dienes. This expectation was based upon a consideration of conjugated diene and/or enamine resonance effects which should stabilize transition states for γ rather than α-protonation of **4**. Support for this view can be found in the results of electrophile additions to related 1-amino and 1-alkoxy substituted allyl anions where selective γ-electrophile capture is reflected in the exclusive or preferential formation of enamine and enol ether products.[11]



3 4 (3)

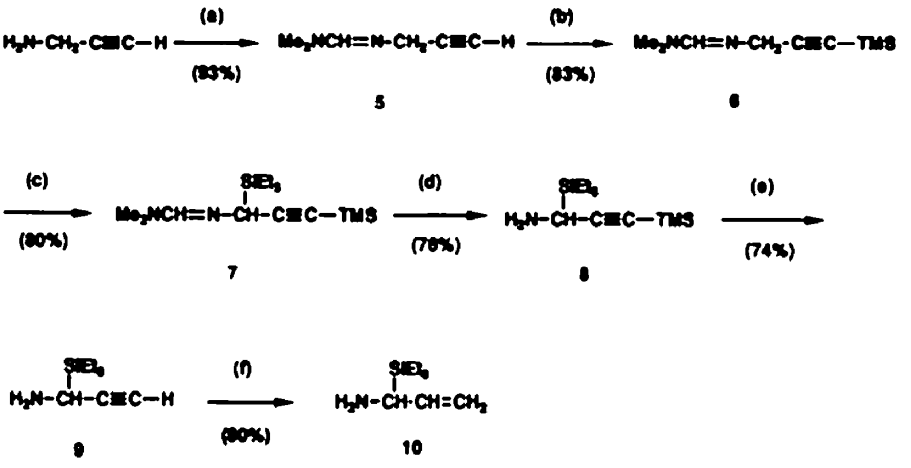
A protodesilylation approach for 2-aza-1,3-diene synthesis would have some obvious advantages over the closely related base-isomerization process. The most important of these relates to the fact that strongly basic conditions are avoided. Consequently, the method would be applicable to a wider range of substrates even those containing acidic α-imino hydrogens. The use of this methodology would of course require the availability of silylallylamine precursors of **3**, a feature which could detract from its generality.

In the discussion that follows, we report the results of an investigation designed to probe the scope, limitations and mechanistic aspects of the protodesilylation route for 2-aza-1,3-diene synthesis outlined in equation 3.[12] During the course of these studies, we have (1) developed a short, modestly efficient sequence for preparation of amine precursors of silylallylimines related to **3**, (2) demonstrated that fluoride-ion induced protodesilylation of substances related to imine **3** leads to generation of 2-aza-1,3-dienes, and (3) shown that the stereochemical course of the azadiene forming process can be controlled by a proper choice of reaction conditions.

Results

Preparation of N-1-Triethylsilyl-2-propenyl Amine 10. The silylallylamine **10** and related acetylene analogs **8** and **9** serve as key intermediates in routes we have developed for synthesis of starting materials in our protodesilylation approach to 2-aza-1,3-dienes. The sequence used for preparation of compounds of this type (Scheme 1) begins with propargylamine and is modeled after a route used by Kolb and Barth[13] for synthesis of α-substituted α-amino acids. Reaction of propargyl amine with N,N-dimethylformamide dimethylacetal provides the amidine **5** in which the amine function is protected for ensuing transformations. The acetylide, generated from **5**, is then reacted with TMSCl to produce the acetylene **6** with a bulky substituent at C-1 to prevent silylation at this position in the subsequently derived propargylic anion. Accordingly, the blocked bis-silyl acetylene **7** is then formed through a sequence involving n-BuLi deprotonation and silylation with triethylsilyl chloride (TESCl). The decision to incorporate a TES-group at the propargylic position was guided by the observed lability of a TMS-substituent under the conditions used for amidine and terminal TMS removal. Conversion of **7** to the mono-silyl propargyl amine **9** was accomplished by deamidination with anhydrous hydrazine in t-butyl alcohol followed by desilylation with lithium ethoxide in ethanol. Catalytic hydrogenation of **9** with the Lindlar catalyst then furnishes the desired silylallyl amine **10**. This sequence is modestly efficient (overall yield of 31%) and appears versatile enough to be extended to the preparation of other amines in this class having a variety of substitution patterns on the allylic moiety.

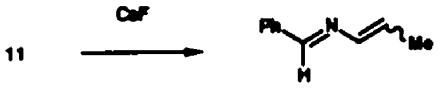
Scheme 1.



(a) $Me_2NCH(OMe)_2$, 25°C; (b) nBuLi, THF/TMSCl, -78°C; (c) nBuLi, THF/TESCl, -78°C; (d) N_2H_2, tBuOH, 25°C; (e) LiOEt, EtOH, 25°C; (f) H_2, Lindlar, THF.

11 (R = Ph)
12 (R = Et)

13 (R = TMS)
14 (R = H)



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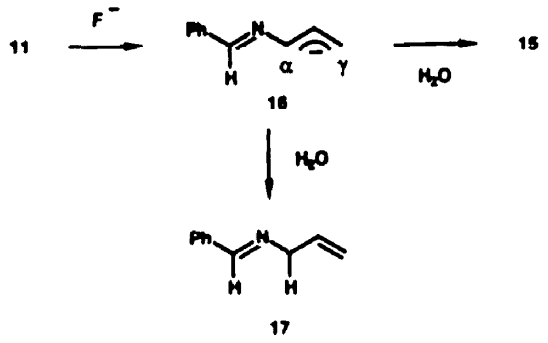
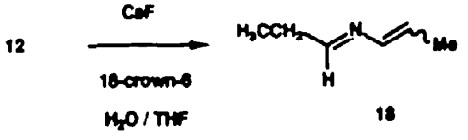
Formation and Protodesilylation of Silyl-Allyl and Propargyl Imines. The silylallyl and silylpropargyl amines **8-10** readily condense with aldehydes to produce the corresponding aldimines **11-14** which are used to probe features of the protodesilylation process. In each case, only a single C-N double bond isomer having the E-configuration was produced.[14] As discussed above, we anticipated that protodesilylation of these systems would serve as an efficient method for 2-aza-1,3-diene synthesis. Indeed, treatment of silylallyl imine **11** with CsF (5 equiv.) in a THF solution containing 18-crown-6 (0.17 equiv.) and a trace amount of adventitious water leads to generation of the known[8] azadiene **15** (80%) as a 6:1 mixture of E,E and E,Z isomers. The stereoisomer ratio was determined by ^1H NMR and glc methods analogous to those reported previously.[8] Alternatively azadiene **15** can be produced as a 1:2 mixture of E,E and E,Z-diastereomers by treatment of **11** with CsF (5 equiv.) in MeCN solution containing 0.06 M H_2O. The variations noted in the stereochemical outcomes of these processes will be addressed at a later point in this publication.

A priori, two possible mechanisms could be responsible for the transformation of **11** to **15**. The first involves fluoride ion induced desilylation to form the imino-allyl anion **16** followed by γ-protonation. Alternatively, α-protonation of **16** generating the N-allylimine **17** could be followed by isomerization under the reaction conditions to **15**. Evidence in support of the former pathway comes from ^1H NMR monitoring of the reaction progress which shows no build-up of **17** and from

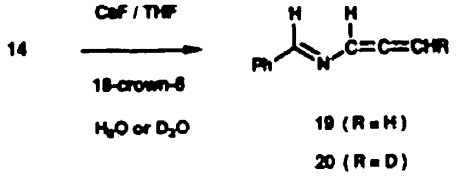
the observation that **17** is unreactive under the conditions used for conversion of **11** to **15**. Furthermore, reaction of **11** with CsF and 18-crown-6 in CD_3CN containing D_2O leads to exclusive formation of mono-γ-deuteriated azadiene stereoisomers.

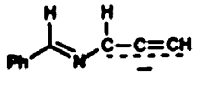


The versatility of the protodesilylation methodology for azadiene synthesis is demonstrated by the transformation of silylallylimine **12** to 1,3-azadiene **18**. It is difficult to evaluate the efficiency of this process owing to the instability of **18**. However, ^1H NMR monitoring of the reaction of **12** with CsF, 18-crown-6 and H_2O in d_8-THF at 25°C showed that azadiene **18** is formed *in situ* in near quantitative yield as a mixture of E,E and E,Z-isomers.



The allene containing 2-azadiene **19** can be generated starting with the silylpropargyl imines **13** and **14**. Thus, treatment of **14** with CsF, 18-crown-6 and H_2O in THF produces the N-allenylimine **19** in a 81% yield. The spectroscopic properties of **19**[15] are in complete accord with the assigned structure. Characteristic signals in the ^1H NMR spectrum at 5.26 (dd), 6.92 (t) and 8.29 (s) ppm corresponding to the respective allene methylene, allene methine and, aldimine protons serve to exemplify this point. In addition, the IR absorption at 1445 cm^{-1} corresponds to the characteristic allene stretching band. In order to show that **19** is the kinetic product of protodesilylation of **14** (see below), reaction was conducted by using CsF, 18-crown-6 and D_2O. ^1H NMR analysis of the product indicated that it was the 5-deuterio-azatriene **20**, thus demonstrating that the allene-containing azadiene **19** arises by γ-protonation of an intermediate propargyl anion **21**.





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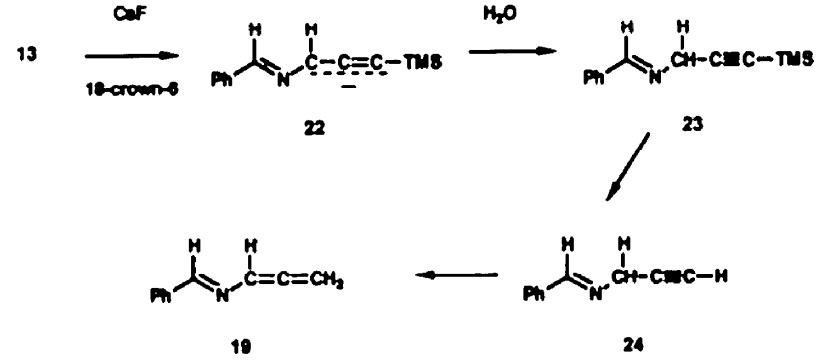
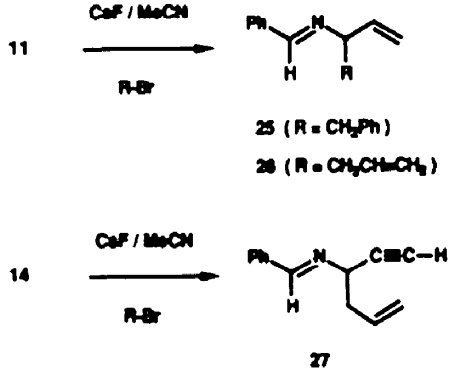
The mechanistic sequence followed in transforming the bis-silylpropargyl imine **13** to azatriene **19** is interesting as a result of it deceptive complexity. Treatment of **13** with excess CsF in THF solution containing 18-crown-6 and H_2O provides **19** in a 75% yield. The nature of this process was revealed by ^1H NMR monitoring the reaction progress which showed that the initially formed (3 min) mono-protodesilylation product is the silylpropargylimine **23**. Thus, it appears that fluoride displacement of the more bulky triethylsilyl grouping in **13** is favored perhaps due to the fact that it leads to generation of a imine-conjugated propargyl anion **22** rather than a more localized acetylide anion. In addition, protonation of **22** appears to occur at the α- rather γ-carbon. Regiocontrol in this case is due to the bulky TMS-group at the γ-position. After a 10 min period **23** is transformed to the propargyl imine **24** which eventually (1h) isomerizes to the allene **19**. Indeed, independently synthesized **24** is converted to **19** by treatment with CsF, 18-crown-6, $ClSiEt_3$, $HClO_4$ in THF, conditions which mimic those present in reaction of **13** to produce **19**.[16]



Alkylative Desilylation of Silylallylimine 11 and Silylpropargylimine 14. Azadiene formation by protodesilylation of the imines **11** and **14** is a result of selective γ-protonation of intermediate imino-allyl and propargyl anions or γ-protodemetallation of their pentavalent silicate equivalents. Interestingly, alkylation reactions of these anions show high degrees of α-regioselectivity. For example, treatment of the imine **11** with CsF in a MeCN solution containing allyl bromide leads to formation of the 3-hexadienylimine **25** (74%) rather than its 1-hexadienyl analog. Similarly, benzylation of **11** occurs under these conditions to produce the alkylation



product **6** exclusively (70%) and propargyl imine **14** affords the α-allylation product **27** in a 73% yield.

Silyl-Allyl Imine 11 Protodesilylation Stereochemistry. As shown above, the stereochemical course of protodesilylation of silylallyl imine **11** appears to be a sensitive function of the reaction conditions. In order to gain further information about this feature, CsF-induced protodesilylations of **11** were conducted under conditions in which solvent, water content and the presence of 18-crown-6 were varied. The results are summarized in Table 1. For reactions of **11** with CsF in THF solutions containing 0.15 equivalents of 18-crown-6, increasing concentrations of

water from trace to 0.5 M causes the E,E:E,Z azadiene 15 stereoisomer ratio to decrease from 6:1 to ca. 1:1. In contrast, increasing water concentration has an opposite effect upon the E,E:E,Z ratio for protodesilylations occurring in MeCN solutions in the absence of 18-crown-6. Addition of the metal cation complexing agent (0.15 equiv.) in this case leads to an increase in the 15 E,E:E,Z ratio.

The stereochemistry of these processes is a result of kinetic rather than thermodynamic factors. Accordingly, the E,E:E,Z ratios (6:1 or 0.3:1) of 15 are unchanged when aqueous THF or MeCN solutions of this substance are stirred for extended time periods. In addition, the observations (see above) that only the mono-deuterium labeled azadiene, $PhCH{=}N\text{-}CH{=}CHCH_2D$ (E,E: E,Z = 1:1) is produced by reaction of 11 with CsF in MeCN containing 18-crown-6 and 0.4 M D_2O suggests that equilibration of the stereoisomers of 15 is not occurring under these conditions.

It is likely that the stereochemical course of protodesilylation of 11 is governed factors which influence conformational preferences in transition states for protonation of the intermediate iminoallyl anion. Interestingly, base catalyzed isomerization of the non-silicon containing N-allylimine 17 most probably proceeds through a similar if not identical allyl anion intermediate. Unfortunately, stereochemical information about this process was not provided in the reports of this chemistry by Wender[9] and Taylor and Worley.[8] As a result of this, we have investigated the stereochemistry of the KOtBu-induced isomerization of 17, placing particular emphasis on the effects of 18-crown-6. As the data in Table 2 suggest, addition of 18-crown-6 results in a pronounced increase in the 15 E,E:E,Z ratio. For example, reaction of 17 with KOtBu in THF containing 0.4 equivalents of 18-crown-6 at -30°C results in a 9:1 E,E:E,Z ratio of 15. Here again, this result is of kinetic origin since azadiene isomerization does not occur at appreciable rates in the presence of KOtBu and 18-crown-6 even at elevated (25°C) temperatures.

Table 1. Silylallylimine 11 Protodesilylation (CsF) stereochemistry.

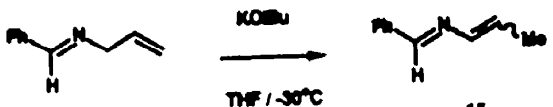
Solvent	Water Concentration (M)	18-crown-6[a]	15 E,E:E,Z Ratio
THF	trace	yes	6.0
THF	0.13	yes	2.0
THF	0.16	yes	1.3
THF	0.30	yes	1.0
THF	0.50	yes	1.0
MeCN	0.03	no	0.3
MeCN	0.06	no	0.5
MeCN	0.06	yes	0.9
MeCN	0.09	no	1.0
MeCN	0.13	no	1.0
MeCN	0.30	no	1.0

(a) 0.15 equivalents relative to 11 and 0.03 equivalents relative to CsF.

Table 2. Allylimine 17 to Azadiene 15 Base-Catalyzed Isomerization Stereochemistry.[a]

18-Crown-6 (equivalents)[b]	15 (E,E:E,Z) Ratio
0.4	9.0
0.3	6.5
0.23	5.4
0.0	0.9

(a) KOtBu / THF / -30°C / 3 min; (b) relative to 17.



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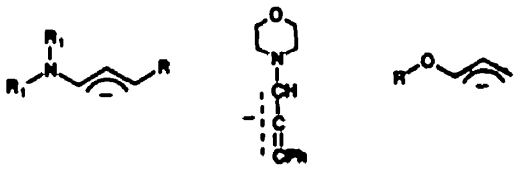
Discussion

General Features. As demonstrated by the examples provided above, the protodesilylation route represents a mild and efficient procedure for 2-aza-1,3-diene synthesis. Unlike, the closely related base-catalyzed process, it is applicable to systems which contain base sensitive functionality. Of course, implementation of this methodology requires that the N-(3-trialkylsilylpropen-3-yl)imines be prepared by convenient preparative sequences. The route presented above (Scheme 1) for synthesis of the triethylsilylallyl amine precursor of these imines, while not the only one conceivable, appears to be sufficiently versatile and efficient. Thus, the protodesilylation methodology should be generally applicable.

Regiochemistry. The regiochemistry of the protodesilylation reactions discussed above requires brief comment. If fluoride-ion induced desilylation reactions of the silylallyl imines (and related acetylenes) proceed via the intermediacy of 1-imino-allyl anions, γ-protonation delivers the 2-azadiene products. The regioselectivities of these processes are analogous to those observed for closely related enamine and vinyl ether forming base-induced isomerizations of respective allylamines and allyl ethers.[7,11] As demonstrated by our deuterium labeling studies, the regiochemical course of those processes is not controlled by thermodynamics. Rather, the greater rates of imino-allyl anion γ-protonation appear to reflect transition state stabilization by enamine or diene resonance (depending on conformation) developing in the forming azadiene.

Observations made in studies with the silylpropargyl imines **13** and **14** suggest that steric factors can also be influential in governing protodesilylation regiochemistry. Accordingly, while the propargyl anion **21** with hydrogen at the γ-carbon undergoes exclusive γ-protonation, the related γ-TMS-substituted anion, **22** is protonated selectively at the α-position to generate the silylpropargyl imine **23**.

In contrast to these observations, we have found that alkylations of the intermediate imino-allyl and -propargyl anions, **16** and **21**, occur exclusively at the α-position. Inspection of results from investigations of electrophile additions to related 1-amino and 1-alkoxy substituted allyl anions shows that the α-alkylation regiochemistry observed in our work, while not unique, is rare. For example, Ahlbrecht[17] has found that 1-amino-allyl anions **28** derived by metalation of enamines undergo γ-alkylation and, thus, serve as homoenolate equivalents. The regioselectivity is maintained even in the cases of the 3-trimethylsilyl-1-amino allyl anions **28** (R=TMS) where steric effects could have favored α-alkylation. Similarly, Craig[18] has shown that the propargyl anion **29** undergoes γ-alkylation by dimethyl sulfate to produce an allenyl-amine. Still[11b] and Evans[11a] have demonstrated independently that lithiated allylic ethers add alkyl halides at both the γ- and α-positions, with the former predominating. The steric bulk of the oxy-substituent, R, in the intermediate anions **30** plays a key role in controlling the γ:α alkylation regioselectivities which increase with increasing size of R.[19]



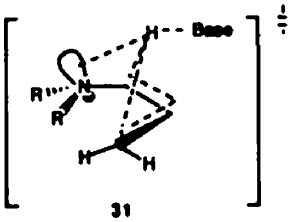
28 29 30

In view of the combined observations, the γ-selectivities seen in the alkylative desilylation reactions of silyl allyl- and propargyl-imines **11** and **14** are not easily rationalized. Steric factors do not seem to be influential since the terminal carbons in the anions derived from these species are

clearly less encumbered. Equally insecure are explanations based upon electronic considerations especially when the differences between alkylation and protonation regiochemistries are considered.[21] In any event, the α-selectivities for these alkylative-desilylation reactions indicate that methods of this type can not be applied to the synthesis of 2-aza-1,3-dienes with complex 4-alkyl side chain substituents. However, an alternative route to substances of this class might be available through alkylation of acetylide anions derived from the propargyl amines and imines related to 9 or 14. Current efforts are underway to probe this issue.

Stereochemistry. Another interesting feature of these studies concerns the stereochemistry of the azadiene 15 forming protodesilylation reactions of silylimine 11 and the related base-induced isomerization of allylimine 17. While the factors influencing the stereochemistry of these processes appear to be complex, several general trends have been noted. For example, reaction of 11 with CsF in THF gives a 6:1 ratio of the E,E and E,Z isomers of 15 when 18-crown-6 is present and water concentrations are low. As the water concentration increases, the E,E: E,Z ratio approaches unity. In contrast, reaction of 11 with CsF in MeCN in the absence of 18-crown-6 at low water concentration yields a mixture of 15 E,E and 15 E,Z with the latter predominating. An increase in water concentration in this case causes an increase in E,E:E,Z ratio which approaches unity at high water concentration. Also, addition of 18-crown-6 results in a modest (2X) increase in the E,E:E,Z ratio when water concentration is low. The stereochemical course of the related KOtBu catalyzed isomerization of allylbenzaldimine 17 is influenced by the metal cation complexing agent. The 15 E,E: 15 E,Z ratio increases from 0.9 to 9.0 upon addition of 0.4 equivalents of 18-crown-6.

The enhanced stereoselectivities observed for the base-catalyzed isomerization of 17 when 18-crown-6 is present can be accounted for on the basis of metal cation effects on conformational preferences in transition-states for protonation of the intermediate 1-imino-allyl anion. In this context, the results of studies probing related base-induced isomerizations of tertiary allylamines appear pertinent. Sauer and Prahl[22] in efforts which have clarified the original studies by Price[23] have shown that isomerization of allylamines by KOtBu in DMSO leads to near exclusive formation of cis-enamines. Similar observation have been made by other workers.[7,11] The cis-enamine selectivity appears to be maintained for reactions conducted using a variety of base/solvent pairs (e.g. $NaNH_2/NH_3$, tBuOK / HMPA). These stereochemical results along with the observation that hydrogen/deuterium exchange does not occur when deuteriated-bases are present in the reaction medium have been explained by Riviere and Lattes[24] in terms of proton-bridged transition states 31. Stabilization of 31 which leads to the cis-enamine was attributed to hydrogen-bonding interactions between the nitrogen lone pair and bridging proton.



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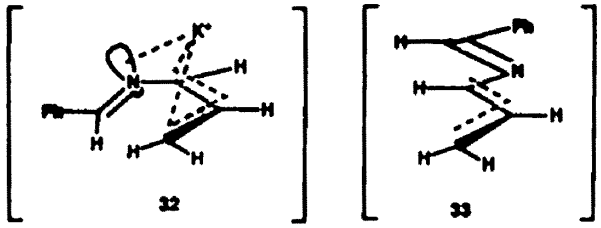
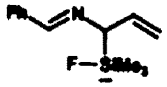
In contrast, the KOtBu (THF) isomerization of 17 in the absence of 18-crown-6 is non-stereoselective. Wender's[9,25] deuterium exchange results coupled with our observation that the azadiene isomers retain their stereochemical integrity under the reaction conditions, suggests that this result has a kinetic origin. These results are in accord with the view that the aldimine isomerization transition states, 32 and 33, which serve as the respective precursors of 15 E,Z and 15 E,E are nearly isoenergetic. Stabilization due to chelate-interactions in 32 is counterbalanced by enhanced conjugation and the relief of steric strain in 33. The location of the tBuOH molecule in both transition states is not specified. Proton bridged structures for 32 and 33 related to 31 but lacking hydrogen-bonding would not be inconsistent with our transition state arguments. When 18-crown-6 is present to externally coordinate the K^+, transition state 32 is no longer available. Thus, the large preference for 15 E,E in this case would reflect the fact that the exo-imino transition state 33 is lower in energy than a non-chelate analog of 32.

Analysis of the protodesilylation reaction stereochemical results is much more difficult since a number of factors including solvent, metal-cation complexing agent and water play a role in this



32 33

process. It is important to note that proton-bridged transition states related to 31 are not involved here since proton delivery occurs externally from water. In addition, it is not clear whether protonation occurs on a pentavalent silicate intermediate 34 or the subsequently formed imino-allyl anions related to 32 (Cs^+ instead of K^+) and 33. Thus, the factors influencing the 15 E,E and 15 E,Z isomer ratios could be operating on several intermediates in this process. What is clear is that protodesilylation of 11 can be controlled to generate either the E,E or E,Z-isomers of 15 preferentially.[26]



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Experimental Section

General. Nuclear magnetic resonance spectra were recorded by using a Bruker WP-200, IBM AM-200 and Bruker AM-400 spectrometers. Chemical shifts are recorded in parts per million relative to tetramethylsilane or $CDCl_3$. In all cases, the solvent for NMR measurements was $CDCl_3$. Infrared spectra were recorded on a Perkin-Elmer 283 or 297 spectrometer. Mass spectrometric data were recorded at 70eV on a Hitachi RMU-6 (low-resolution) or VG-7070 (high-resolution) instruments or at the Pennsylvania State University Mass Spectrometry Center. Melting points were obtained by use of a Mel-temp apparatus and are reported uncorrected. All reactions were run under N_2 atmosphere. Drying of organic solutions obtained during workup of reaction mixtures was over anhydrous sodium sulfate. Preparative TLC was performed on 20X20 cm plates coated with E-Merck Silica gel 60 GF-254. Flash column chromatography was performed with EM-60 silica gel (230-400 mesh). Column chromatography was with MCB Alumina (Type F-20). Molecular distillations were performed at reduced pressure with a Kugelrohr apparatus. HPLC separations were performed on a Whatman reverse phase column (Partisil, ODS-2).

3-(N,N-Dimethylamidino)propyne (5). N,N-Dimethylformamide dimethylacetal (35.4 g, 0.30 mol) was slowly added to propargyl amine (16.4 g, 0.30 mol) at 25°C over a 15 min period. The resulting mixture was stirred at reflux for 3h and then vacuum distilled to give 30.1g (92%) of the desired amidine 5, bp. 85-95°C / 40mm: ^{1}H NMR 2.33 (t, 1H, J=2.4 Hz, acetylene), 2.87 (s, 6H, -N-CH_3), 4.08 (d, 2H, J=2.4 Hz, methylene), 7.5 (s, 1H, vinyl); ^{13}C NMR 36.3 ($N(CH_3)_2$), 41.9 (CH_2), 71.6 (C≡C-H), 81.9 (C≡C-H), 155.5 (C=N); IR ($CHCl_3$), 3300, 2950, 1490 cm^{-1}; high resolution mass spectrum, m/e 110.0846 ($C_6H_{10}N_2$ requires 110.0848).

3-(N,N-Dimethylamidino)-1-trimethylsilylpropyne (6). To a cooled solution (-78°C) of 10.0 g (0.09 mol) of the amidine 5 in 250 mL of THF was slowly added 60.6 mL of a 1.50 M solution of n-butyllithium in hexane. The reaction mixture was stirred for 15 min and 12.7 mL (0.10 mol) of trimethylsilyl chloride was added rapidly. The resulting solution was stirred for 30 min at -78°C, warmed to 25°C, and stirred for an additional 30 min. The reaction mixture was poured into 5% aqueous $NaHCO_3$ and extracted with $CHCl_3$. The organic extracts were dried and concentrated *in vacuo* giving a residue which was vacuum distilled, giving 13.6 g (83%) of the acetylenic amidine 6, bp. 70-80°C / 1 mm: ^{1}H NMR 0.10 (s, 9H, -$SiCH_3$), 2.79 (s, 6H, -N-CH_3), 4.00 (S, 2H, methylene), 7.42 (s, 1H, vinyl); ^{13}C NMR -0.1 ($SiCH_3$), 36.9 (NCH_3), 43.5 (CH_2), 88.7 (C≡C-Si), 155.9 (C=N); IR

($CHCl_3$) 2960, 2170, 1649, 1375 cm^{-1}; high resolution mass spectrum m/e 182.1235 ($C_9H_{18}N_2Si$ requires 182.1233).

3-(N,N-Dimethylamidino)-1-trimethylsilyl-3-triethylsilylpropyne (7). To a cooled solution (-78°C) of 10.0 g (0.06 mol) of the amidine 6 in 250 mL of anhydrous THF was slowly added 33.45 mL of 1.70 M solution of n-butyllithium in hexane. The reaction mixture was stirred for 15 min at -78°C and 9.31 mL (0.06 mol) of triethylsilylchloride was added rapidly. The resulting solution was stirred for 30 min at -78°C, warmed to 25°C, and stirred for an additional 30 min. The reaction mixture was poured into 5% aqueous $NaHCO_3$ and extracted with $CHCl_3$. The organic extracts were dried and concentrated *in vacuo* giving after molecular distillation 13.02 g of the desired amidine 7 (80%), bp. 105-115°C/0.05 mm: ^1H NMR 0.15 (s, 9H, -$SiCH_3$), 0.62 (q, 6H, -$SiCH_2$), 0.93 (t, 9H, -$SiCH_2$ CH_3), 2.80 (s, 6H, NCH_3), 3.94 (s, 1H, CH), 7.45 (s, 1H, CH=N); ^{13}C NMR 0.2 ($SiCH_3$), 2.1 ($SiCH_2$), 7.2 ($SiCH_2CH_3$), 37.0 (NCH_3), 44.2 (N-C-Si), 99.9 (C=C-Si), 106.5 (C=C-Si), 153.1 (C=N); IR ($CHCl_3$) 2970, 2150, 1640, 1380 cm^{-1}; high resolution mass spectrum m/e 296.2102 ($C_{15}H_{32}N2Si_2$ requires 296.2104).

3-Amino-3-triethylsilyl-1-trimethylsilylpropyne (8). A mixture of 5.0 g (17 mmol) of the amidine 7 and 2.7 mL (84 mmol) of anhydrous hydrazine in 30 mL of t-butyl aclohol was stirred at 25°C for 15h. The reaction mixture was poured into 5% aqueous $NaHCO_3$ solution and extracted with $CHCl_3$. The organic extracts were dried and concentrated in vacuo giving a residue which was vacuum distilled to give 3.1 g (76%) of the desired propargylic amine 8, bp 70-75°C/0.025 mm: ^1H NMR 0.10 (s, 9H, $SiCH_3$), 0.68 (q, 6H, $SiCH_2$), 0.9 (t, 9H, $SiCH_2CH_3$), 1.46 (bs, 2H, NH_2), 3.11 (s, 1H, N-CH); ^{13}C NMR -0.1 ($SiCH_3$), 1.9 ($SiCH_2$), 7.1 ($SiCH_2CH_3$), 31.4 (CHSi), 87.2 (C=C-Si), 110.6 (C=C-Si); IR ($CHCl_3$) 3370, 2960, 2160, 1600, 1250 cm^{-1}; This substance is too labile to obtain accurate high resolutin mass specroscopic data.

3-Amino-3-triethylsilylpropyne (9). To a solution of 3.0 g (13 mmol) of the amine 8 in 30 mL of anhydrous ethanol was added 4.1 mL (25 mmol) of a 0.61 M solution of lithium ethoxide in ethanol with stirring at 25°C for 10h, poured into 5% aqueous $NaHCO_3$ solution and the mixture was extracted with $CHCl_3$. The $CHCl_3$ extracts were dried and concentrated in vacuo giving a residue which was vacuum distilled to give 1.6 g (75%) of the silylpropargyl amine 9, bp. 30-45°C/ 0.025 mm: ^1H NMR 0.67 (q, 6H, $SiCH_2$), 1.01 (t, 9H, $SiCH_2CH_3$), 2.30 (bs, 2H, NH), 2.30 (d, 1H, J=2.6 Hz, =C-H), 312 (d, 1H, J=2.6 Hz, N-CH-Si; ^{13}C NMR 1.9 ($SiCH_2$), 7.2 ($SiCH_2CH_3$), 30.7 (CH-Si), 88.2 (C=C-H), 97.5 (C=C-H); IR 3300, 2890, 2100, 1557, 1410 cm-1; due to the instability of this compound accurate mass spectroscopic data cannot be obtained.

N-1-Triethylsilylprop-2-en-1-ylamine (10). A pre-equilibrated mixture of Lindlar's catalyst (450 mg) and propynylamine 9 (2.0g, 12 mmol) in 25 mL of THF was stirred at 25°C under 1 atm of hydrogen until 1 equivalent of hydrogen had been absorbed. Filtration gave a filtrate which was concentrated *in vacuo* giving a residue which was vacuum distilled to give 1.8 g (90%) of the allylic amine 10, bp 60-70°C/1 mm: ^1H NMR 0.59 (q, 6H, $SiCH_2$), 1.00 (t, 9H, $SiCH_2CH_3$), 1.40 (bs, 2H, NH), 3.14 (d, 1H, N-CH-Si), 5.02 - 4.86 (m, 2H, $=CH_2$), 6.01-5.94 (m, 1H, -CH=). ^{13}C NMR 1.5 ($SiCH_2$), 7.1 ($SiCH_2CH_3$), 44.7 (N-C-Si), 108.6 ($HC=CH_2$), 142.0 ($HC=CH_2$); IR ($CHCl_3$) 3350, 2970, 1635, 1020, 900, 850 cm^{-1}; high resolution mass spectrum m/e 171.1437 ($C_9H_{21}NSi$ requires 171.1443).

N-(3-Triethylsilylpropen-3-yl)benzaldimine (11). A solution of benzaldehyde (99 mg, 0.93 mmol) and 3-triethylsilylpropen-3-ylamine (10) (160 mg, 0.93 mmol) in 60 mL anhydrous benzene was stirred at reflux for 14h. Removal of water was accomplishted by use of soxhlet apparatus with molecular seives (type 4A). The reaction mixture was concentrated *in vacuo* giving an oil which was subjected to column chromatography on alumina ($CHCl_3$) yielding 223 mg (90%) of the benzaldimine 11: ^1H NMR 0.98 (q, 6H, $SiCH_2$), 1.03 (t, 9H, $SiCH_2CH_3$), 4.02 (d, 1H, NCH-Si), 4.92-5.15 (m, 2H, $C=CH_2$), 6.15 - 6.32 (m, 1H, $C=CH_2$). 7.37-7.74 (m, 5H, aromatic), 8.14 (s, 1H, CH=N); ^{13}C NMR 1.6 ($SiCH_2CH_3$), 7.2 ($SiCH_2$), 67.9 (NCH-Si), 110.7 ($CH=CH_2$), 127.5, 128.3,

129.6 136.7, 138.09 (CH=CH_2), 155.4 (C=N); IR ($CHCl_3$) 2960, 2880, 1640, 1630, 1460, 1020 cm^{-1}; high resolution mass spectrum m/e 259.1757 ($C_{16}H_{25}NSi$ requires 259.1787).

N-(3-Triethylsilylpropen-3-yl)propionaldimine (12). A solution of propinoaldehyde (342 mg, 5.9 mmol), the propenylamine **10** (100 mg, 0.6 mmol), and molecular seives (type 4A) in 10 mL of anhydrous benzene was stirred at 0°C for 1h. The reaction mixture was filtered and concentrated *in vacuo* giving 103 mg (83%) of crude (> 90% purity) propionaldimine **12**: ^1H NMR 0.57 (q, 6H, $SiCH_2$), 0.94 (t, 9H, $SiCH_2CH_3$), 1.04 (t, 3H, methyl), 2.20 (m, 2H, methylene), 3.69 (d, 1H, N-CH), 4.48 (m, 2H, C=CH_2), 6.09 (m, 1H, CH=C), 7.48 (t, 1H, CH=N); ^{13}C NMR 1.6 ($SiCH_2$), 7.2 ($SiCH_2CH_3$), 12.0 (CH_3), 29.5 (CH_2), 67.9 (CHSi), 110.8 (CH=CH_2), 139.0 (CH=CH_2), 161.0 (CH=N); IR ($CHCl_3$) 2950, 1730, 1660, 1460, 1260, 1010 cm^{-1}; high resolution mass spectrum m/e 210.1674 ($C_{12}H_{24}NSi$ requires 210.1654).

N-(3-Triethylsilyl-1-trimethylsilylpropyn-3-yl)-benzaldimine (13). A solution of benzaldehyde (44 mg, 0.41 mmol) and 3-triethylsilyl-1-trimethylsilylpropyn-3-ylamine **8** (100 mg, 0.41 mmol) in 60 mL anhydrous benzene was stirred at reflux for 5h. Removal of water was accomplished by use of a solvent apparatus with molecular seives (type 4A). The reaction mixture was concentrated *in vacuo* giving an oil which was subjected to column chromatography on alumina ($CHCl_3$) yielding 124 mg (92%) of the benzaldimine **13**: ^1H NMR (THF-d_8) 0.22, 0.23 (s, 9H, $SiCH_3$), 0.76 (q, 6H, $SiCH_2$), 1.06 (t, 9H, $SiCH_2$), 4.51, 4.56 (d, 1H, -CH-), 7.36-7.76 (m, 5H, aromatic), 8.56 (d, 1H, CH=N); ^{13}C NMR 0.1 ($SiCH_3$), 2.0 ($SiCH_2$) 7.2 ($SiCH_2CH_3$), 50.4 (N-C-Si), 94.9 (=C-Si), 103.2 (C$\equiv$C-C), 127.7, 128.4, 129.83, 136.7, 157.2 (C=N); IR ($CHCl_3$) 2950, 2860, 2160, 1690, 1640, 1450 cm^{-1}; high resolution mass spectrum, m/e 329.1997 ($C_{19}H_{31}NSi_2$ requires 329.2057).

N-(3-Triethylsilylpropyn-3-yl)benzaldimine 14. A solution of benzaldehyde (162 mg, 0.56 mmol) and 3-triethylsilylpropyn-3-y lamine **9** (100 mg, 0.59 mmol) in 60 mL of benzene was stirred at reflux for 5h. Removal of water was accomplished by use of a soxhlet apparatus with molecular seives (type 4A). The reaction mixture was concentrated *in vacuo* giving 136 mg (90%) of the benzaldimine **14**: ^1H NMR 0.90 (q, 6H, $SiCH_2$), 1.03 (t, 9H, $SiCH_2CH_3$), 2.60 (d, 1H, C=CH), 4.35 (t, 1H, NCHSi), 7.26-7.80 (m, 5H, aromatic), 8.35 (d, 1H, CH=N); ^{13}C NMR 2.2 ($SiCH_2$), 7.2 ($SiCH_2CH_3$), 49.5 (N-CH), 76.3 (C=CH), 81.3 (C=CH), 127.8, 128.5, 129.9, 137.0, 157.3 (CH=N); IR ($CHCl_3$) 3300, 3020, 2950, 2880, 2400, 1700, 1630, 1570, 1450, 1425 cm^{-1}; high resolution mass spec, m/e 257.1585 ($C_{16}H_{23}NSi$ requires 257.1530).

1-Phenyl-2-aza-1,3-pentadiene 15. A solution of the benzaldimine **11** (100 mg, 0.39 mmol), 18-crown-6 (15 mg, 0.06 mmol), and CsF (296 mg, 1.95 mmol) in 4 mL of THF was stirred at 25°C for 8h. The reaction mixture was poured into distilled water and extracted with $CHCl_3$. The $CHCl_3$ extracts were dried and concentrated *in vacuo* giving 45 mg (80%) of a product mixture which contained the E,E and E,Z isomers of **15** in 6:1 ratio. The spectrascopic data for these substances match those previously reported.[8]

Stereochemistry of the Benzaldimine 11 to Azadiene 15 Transformation. Solutions of the benzaldimine **11** (50 mg, 0.20, mmol), 18-crown-6 (7 mg, 0.03 mmol) and CsF (147 mg, 1.0 mmol) in THF solutions containing different concentration of H_2O (0.13M, 0.16M, 0.30M, 0.50M) were stirred at 25°C for 8h. The reaction mixtures were poured into distilled water and extracted with $CHCl_3$. The $CHCl_3$ extracts were dried and concentrated *in vacuo* giving product mixtures which were analyzed (^1H NMR methods (integrations of Me-proton resonances at 1.85 ppm (E:E) and 2.05 ppm (E,Z)) to determine the E:Z isomer ratios in the azadienes **15**. The E,Z isomer ratios for H_2O concentrations of 0.13M, 0.16M, 1.30M are recorded in Table 1.

Solutions of the benzaldimine **11** (50 mg, 0.20 mmol) and CsF (147 mg, 0.10 mmol) in CH^3CN containing different concentrations of H_2O (0.06M, 0.09M, 0.13M, 0.30M) were stirred at 25°C for 16h. The reaction mixtures were poured into distilled water and extracted with $CHCl_3$. The $CHCl_3$

extracts were dried and concentrated *in vacuo* giving product mixtures which were analyzed by ^1H NMR. The E,Z isomer ratios for **15** from reactions with water concentrations 0.06M, 0.09M, 0.13M, 0.30M are recorded in Table1.

Stereochemistry of Base-Catalyzed Isomerization of N-Allylbenzaldimine (17) to Azadiene 15. Solutions (THF) of benzaldimine **17**, KOtBu (0.3 equiv.) and 18-crown-6 (from 0 to 0.4 equiv.) were stirred at -30°C for 3 min and then poured into water. The $CHCl_3$ extracts of these solutions were dried and concentrated *in vacuo* giving residues which were analyzed by ^1H NMR (intergration of Me-proton resonances at 1.85 (E,E) and 2.05 ppm (E,Z)) to determine the **15** E,E:E,Z ratios. The results are recorded in Table 2.

4-Aza-3,5-heptadiene (18). A mixture of the propionaldimine **12** (71 mg, 0.34 mmol), CsF (258 mg, 1.7 mmol), 18-crown-6 (13 mg, 0.05 mol) and H_2O (6.1 uL, 0.34 mmol) in 1 mL of d_8-tetrahydrofuran was agitated in an NMR tube over a period of 1h at 25°C. ^1H NMR analysis showed the formation of an isomeric mixture of 4-aza-3,5-heptadiene **18**: E,Z-isomer: ^1H NMR (THF-d_8), 1.05 (t, 3H, $-CH_2\underline{CH_3}$), 1.68 (d, 3H, $=C-CH_3$), 2.20 (m, 2H, methylene), 5.25 (quint, 1H, C=CH-), 6.45 (d, 1H, NCH=), 7.55 (t, 1H, -CH=N); E,E-isomer: 1.05 (t, 3H, $-CH_2\underline{CH_3}$), 1.82 (d, 3H, $=C-CH_3$), 2.20 (m, 2H, methylene), 5.78 (m, 1H, C=CH-), 6.55 (d, 1H, NCH=), 7.60 (t, 1H, -CH=N). The instability of this substance prevented the accumulation of additional spectroscopic data.

1-Phenyl-2-aza-1,3,4-pentatriene (19). From Silylpropargylimine 14. A solution of the imine **14** (100 mg, 0.39 mmol), 18-crown-6 (15 mg, 0.06 mmol), H_2O (7 uL, 0.39 mmol), and CsF (296 mg, 1.95 mmol) in 4 mL of THF was stirred at 25°C for 1h. The reaction mixture was poured into distilled water and extracted with $CHCl_3$. The $CHCl_3$ extracts were dried and concentrated *in vacuo* to give 45 mg (81%) of the azatriene **19**: ^1H NMR 5.34 (dd, 2H, J=6.0, 1.7 Hz, $C=CH_2$), 6.89 (t, 1H, J=6.0 Hz, -CH=C), 7.30-7.8 (m, 5H, aromatic), 8.26 (s, 1H, CH=N). ^{13}C NMR 81.2 ($=CH_2$), 112.2 (N-CH=), 128.8, 128.9, 130.9, 134.2, 160.0 (CH=N), 193.4 (=C=); IR ($CHCl_3$) 2950, 2880, 1945, 1610, 1580, 1055, 870 cm^{-1}. Owing to the instability of this substance, elemental or high resolution mass spectrometric analysis was not performed.

19 From the Bis-Silylpropargylimine 13. A solution of the imine **13** (123 mg, 0.37 mmol), 18-crown-6 (16.0 mg, 0.06 mmol), H_2O (6.7 uL, 0.37 mmol) and CsF (28 mg, 1.85 mmol) in 4 mL of THF was stirred at 25°C for 30 min. Work up gave 40 mg (75%) of azatriene **19**.

N-(3-Benzylpropen-3-yl)benzaldimine (25). A solution of the silylallylimine **11** (100 mg, 0.39 mmol), benzyl bromide (132 mg, 0.77 mmol) and CsF (291 mg, 1.9 mmol) in 2 mL of anhydrous acetonitrile was stirred at 25°C for 16h. The reaction mixture was poured into distilled water and extracted with $CHCl_3$. The $CHCl_3$ extracts were dried and concentrated *in vacuo* giving an oil which was subjected to separation on HPLC (20% H_2O in MeOH), giving 63 mg (70%) of the benzaldimine **25**: ^1H NMR 2.95 (d, 2H, methylene), 4.15 (td, 1H, NCH-), 5.24 (m, 2H, $=CH_2$), 6.20 (m, 1H, -CH=), 7.20-7.85 (m, 10H, aromatic), 7.96 (s, 1H, CH-N). Owing to the instability of this substance, additional spectroscopic data were not obtained.

N-(3-Allylpropen-3-yl)benzaldimine (26). A solution of the silylallylimine **11** (100 mg, 0.39 mmol), allyl bromide (459 mg, 3.8 mmol), and CsF (293 mg, 1.9 mmol) in 2 mL of anhydrous acetonitrile was stirred at 25°C for 16h. The reaction mixture was poured into distilled water and extracted with $CHCl_3$. The $CHCl_3$ extracts were dried and concentrated *in vacuo* giving an oil which was subjected to preparative GLC (15% carbowax on chromosorb 20W, 2.5 ft X 5/16 in, 150°C, 120 mL/min flow rate), giving 53 mg (74%) of the benzaldimine **26**: ^1H NMR 2.47 (t, 2H, CH2-CH=), 3.80 (td, 1H, N-CH-), 5.20 (m, 4H, $=CH_2$), 5.80 (m, 1H, CH=), 6.10 (m, 1H, CH=), 7.25-7.79 (m, 5H, aromatic), 8.25 (d, qH, CH=N); IR ($CHCl_3$), 3000, 2980, 1640, 1590, 1210, 920, 800 cm^{-1}; high resolution mass spectrum m/e (M^+ - 41) 144.0808 ($C_{10}H_{10}N$ requires 144.0770).

N-(3-Allylpropyn-3-yl)benzaldimine (27). A solution of the imine **14** (100 mg, 0.39

mmol), allyl bromide (440 mg, 3.8 mmol), and CsF (296 mg, 1.9 mmol) in 2 mL of anhydrous acetonitrile was stirred at 25°C for 16h. The reaction mixture was poured into distilled water and extracted with $CHCl_3$. The $CHCl_3$ extracts were dried and concentrated *in vacuo* giving an oil which was subjected to HPLC (20% H_2O in MeOH), giving 52 mg (73%) of the benzaldimine **27**; ^1H NMR 2.51-2.70 (m, 2H, CH2-C=), 2.58 (d, 1H, ≡C-H), 4.51 (td, 1H, NCH-), 5.12-5.30 (m, 2H, $=CH_2$), 5.78-5.95 (m, 1H, CH=), 7.28-7.78 (m, 5H, aromatic), 8.54 (d, 1H, CH=N). Owing to the instability of this substance additional spectroscopic data were not obtained.

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(15) This compound has been previously reported (ref 9) without spectroscopic characterization.

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(25) Isomerization of **17** to **15** conducted with KOtBu (THF) in the presence of 7 mol equiv of tBuOD leads to 33% d_1 -**15** and 67% d_0-**15** (ref 9).

(26) The explanations put forth in the original communication (ref 12) are interesting but seem less compelling at this time.