Stereoselective Synthesis of *trans*-2-Aryl-3-(2-pyridyl)aziridines from an α-Silyl Carbanion[1]

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Five *para*-substituted benzaldehyde oxime *O*-methyl ethers (**3**) [Ar = phenyl, *p*-chlorophenyl, *p*-tolyl, *p*-methoxyphenyl, *p*-(*N*,*N*-dimethylamino)phenyl] reacted with 2-(trimethylsilylmethyl)pyridine (**1**) in the presence of lithium di-isopropylamide (LDA) in tetrahydrofuran to give the corresponding *trans*-2-aryl-3-(2-pyridyl)aziridines (**4**) in high yield (80, 85, 60, 58, and 74%, respectively), with small amounts of (*Z*)-1-amino-1-aryl-2-(2-pyridyl)ethenes (**5**), and *N*′,*N*′-di-isopropylbenzamidines (**7**) as by-products. The yields of compounds (**4**) and (**5**) and their ratio [(**4**) : (**5**)] were considerably influenced by experimental conditions (especially molar ratio and the addition method of the reactants). When treated with LDA, compounds (**3**) were quantitatively converted into benzonitriles, which reacted with anion (**2**) to give enamines (**5**) after elimination of a trimethylsilyl group from the corresponding *N*-trimethylsilyl derivatives, or with additional LDA to give the benzamidine (**7**); aziridines (**4**) were not transformed into enamines (**5**) by the action of LDA. On the basis of these results, a reaction mechanism has been discussed for the formation of compounds (**4**).

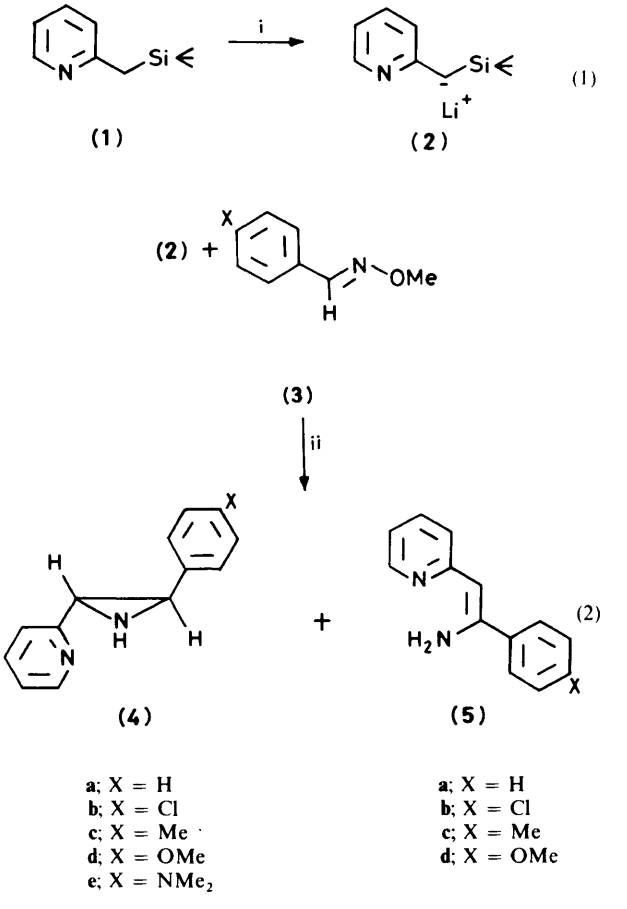
Recently, aziridine derivatives have attracted considerable attention because of their easy conversion into high polymers, their use as aminoalkylating agents, and their powerful physiological actions, including their carcinostatic activity,[2] mutagenicity,[3] antibacterial activity,[4] and antitumour activity.[5] Generally, aziridine derivatives are prepared from (i) β-amino alcohols, (ii) ketoximes and excess of Grignard reagents, (iii) 1,2,3-triazolines, (iv) benzyl ketoximes and lithium aluminium hydride, or (v) alkenes and nitrenes (or imines and carbenes).[2,6,7] The fourth reaction is stereoselective, but the yield is not so high as for the other four routes.

In the course of our investigations of the reactions of α-silyl carbanions with carbonyl compounds or their analogues, and of the biological activities of the products, we have reported that lithiated 2-(trimethylsilylmethyl)pyridine reacted with imines to give (*E*)-2-alkenylpyridines stereospecifically,[8] with benzaldehyde methyl(phenyl)hydrazone to give (*Z*)-β-(2-pyridyl)-styrene at low temperature but predominantly the *E* isomer under reflux,[9] and with benzonitriles to give (*E*)-β-(2-pyridyl)-α-(trimethylsilylamino)styrenes under kinetically controlled conditions and the *Z* isomers under thermodynamically controlled conditions.[10,11] Furthermore, these *N*-silyl enamines reacted with ethyl chloroformate to give a mixture of ethyl (*E*)- and (*Z*)-1-aryl-2-(2-pyridyl)vinylcarbamates, which show insecticidal and/or fungicidal activity.[12]

As an extension of these investigations, in this paper we report a method of preparing stereoselectively *trans*-2-aryl-3-(2-pyridyl)aziridines from an α-silyl carbanion and benzaldehyde oxime *O*-methyl ether or its *para*-substituted derivatives in high yields. A mechanism for the reaction is proposed.

Results and Discussion

As previously reported,[13] 2-(trimethylsilylmethyl)pyridine (**1**) is easily deprotonated by lithium di-isopropylamide (LDA) in tetrahydrofuran (THF) at −78 °C to give an α-silyl carbanion (**2**) [equation (1)]. This anion (**2**) reacted with benzaldehyde oxime *O*-methyl ether or its *para*-substituted derivatives (**3a**—**e**) to give stereoselectively *trans*-2-aryl-3-(2-pyridyl)aziridines (**4**) together with (*Z*)-1-amino-1-aryl-2-(2-pyridyl)ethenes (**5**) as a by-product [equation (2)]. The reaction was performed in three different ways. First, a THF solution of a compound (**3**) was added to a THF solution of the anion (**2**) at −80 to −90 °C (method A). This method, however, gave unsatisfactory results, as described in the preliminary communication;[1] that is, the yield of aziridine (**4**) was low and a considerable amount of enamine (**5**) was formed. Furthermore, the yields of compounds



Reagents and conditions: i, LDA, THF, −78 °C; ii, −80 to −90 °C

Table 1. Reaction conditions and yields of compounds (**4a**) and (**5a**) for Method A

Run	Addition duration of (**3a**)[a]	Conditions[b]		Yield (%)		
		T/°C	t/min	(**4a**)	(**5a**)	PhCHO
1	5 min	−90	60	38	11	6
		rt	120			
2	5 min	−82	2	9	15	20
		−32	12			
3	All at once	−90	60	7	20	15
		rt	120			
4	All at once	−90	60	7	15	28
		0	18			
5[c]	6 min	−90	60	8	31	10
		rt	120			
6[d]	6 min	−90	60	17	16	14
		rt	120			

[a] (**1**) (25 mmol) used; molar ratio (**1**):(**3a**) = 1:1. [b] rt denotes room temperature. [c] Molar ratio (**1**):LDA = 1:1.2. [d] Molar ratio (**1**):(**3a**) = 1:1.5.

Table 2. Yields of compounds (**4**) and (**5**) in Method B

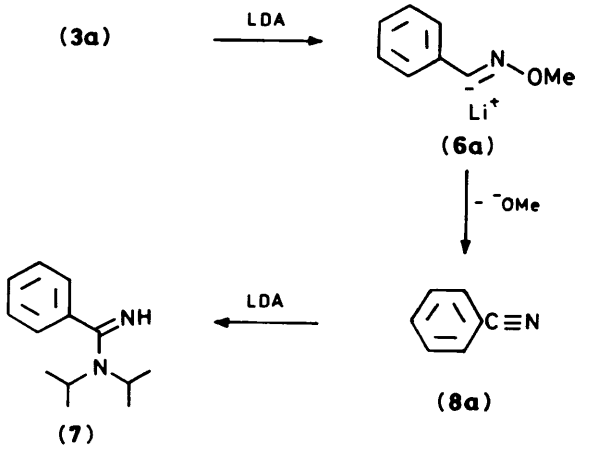
	X	Yields (%)[a,b] (**4**)	(**5**)
(**a**)	H	80 (70)	6
(**b**)	Cl	85 (83)	2
(**c**)	Me	60 (60)	9
(**d**)	OMe	58 (11)	12
(**e**)	NMe_2	74	

[a] Yields based on initial amount of (**1**). [b] Determined by ^{1}H n.m.r. spectroscopy; yield of pure product isolated by column chromatography in parentheses.

(**4**) and (**5**) varied with reaction conditions (Table 1). When compound (**3a**) was slowly added to the solution of anion (**2**) and the resultant mixture was stirred for 1 h at −90 °C and for 2 h at room temperature, the yields of compounds (**4a**), (**5a**), and benzaldehyde were 38, 11, and 5%, respectively (run 1). However, rapid addition of compound (**3a**), and a shorter reaction time, resulted in a decrease in the yield of the aziridine (**4a**) and in an increase in the yields of the enamine (**5a**) and benzaldehyde. In addition, excess of LDA or (**3a**) also gave unsatisfactory results (runs 5 and 6). On the other hand, neither water nor saturated aqueous ammonium chloride, employed as a quencher in method A, had any effect on the yields of compounds (**4a**) and (**5a**).

Secondly, the THF solution of anion (**2**) was added to the THF solution of compound (**3**) at between −80 and −90 °C and the mixture was stirred for 3 h at between −80 and −90 °C and for an additional 2 h at room temperature (method B). As a result, the aziridines (**4a**—**e**) were selectively obtained in high yield (58—85% determined by ^{1}H n.m.r. spectroscopy), and the formation of enamines (**5**) was strongly suppressed (2—12% yield, Table 2). However, the *p*-*N*,*N*-dimethylamino derivative of the aziridine, (**4e**), was highly unstable and could not be isolated by column chromatography on Florisil or by preparative high-pressure liquid chromatography (h.p.l.c.) on Florisil (or Shodex polymer HP-125).

Finally, a mixture of compounds (**1**) and (**3a**) was treated with an equimolar solution of LDA in THF at −80 °C for 3.5 h and for an additional 4 h at room temperature (method C). No aziridine (**4a**), however, was formed at all, but the enamine (**5a**) was obtained in 12% yield, together with *N*′,*N*′-di-isopropylbenzamidine [(**7**), 27% yield], and the unchanged starting materials (**1**) (74%) and (**3a**) (12%). In order to determine the mechanism for the formation of products (**5a**) and (**7**), the following three reactions were performed. First, when the oxime *O*-methyl ether (**3a**) was treated with LDA in THF under the conditions mentioned above, benzonitrile (**8a**) was formed in 67% yield by elimination of methoxide ion from a methoxyimino carbanion (**6a**) (Scheme 1).[14] This reaction is analogous



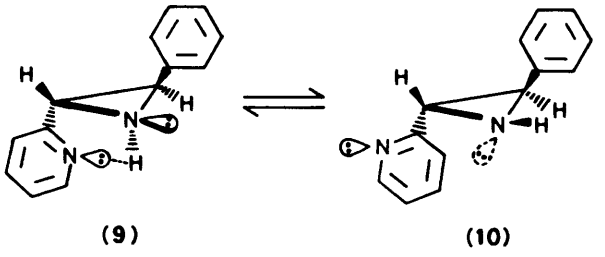
Scheme 1.

to that of a Schiff's base with LDA to form an imino carbanion.[15] Secondly, benzonitrile (**8a**) reacted with LDA to give the corresponding adduct (**7**), in 73% yield (see Experimental section).[16] On the other hand, it has been reported that benzonitrile (**8a**) reacts with anion (**2**) to give a mixture of (*E*)- and (*Z*)-β-(2-pyridyl)-α-(trimethylsilylamino)styrene in high yield.[10] If this *N*-silyl enamine selectively eliminates a trimethylsilyl group by the action of lithium methoxide which may be generated from (**6a**), one of the by-products, (**5a**), would be formed. In order to confirm this hypothesis, an authentic sample of the *N*-silyl enamine was treated with lithium methoxide to give thermodynamically stable (**5a**) in high yield (the third reaction). These results show that benzonitrile (**8a**), generated from compound (**3a**) by the action of LDA or anion (**2**), is an intermediate in the preparation of compounds (**5a**) and (**7**).

The structure of compounds (**4**), (**5**), and (**7**) was determined by their spectroscopic properties and by elemental analyses (Experimental section). For example, the i.r. spectrum of the aziridine (**4a**), measured in a KBr disc, suggested the presence of the hydrogen-bonded NH group at 3 230 cm^{-1} in addition to an aziridine ring (1 210 and 855 cm^{-1} for ν_s and ν_{as} of CH), but the *cis* isomer exhibits[17] an absorption band of the free NH group at 3 317 cm^{-1}. This suggests that the inversion of the nitrogen atom in compound (**4a**) may be fixed in the form (**9**) in the solid state because of the intramolecular hydrogen bond (Scheme 2). In carbon tetrachloride (2.5×10^{-1}—2.5×10^{-3} M solution) at room temperature, however, the absorption band of compound (**4a**) was observed at 3 260 cm^{-1} with a shoulder at 3 230 cm^{-1}, and the position of these bands was independent of concentration.*

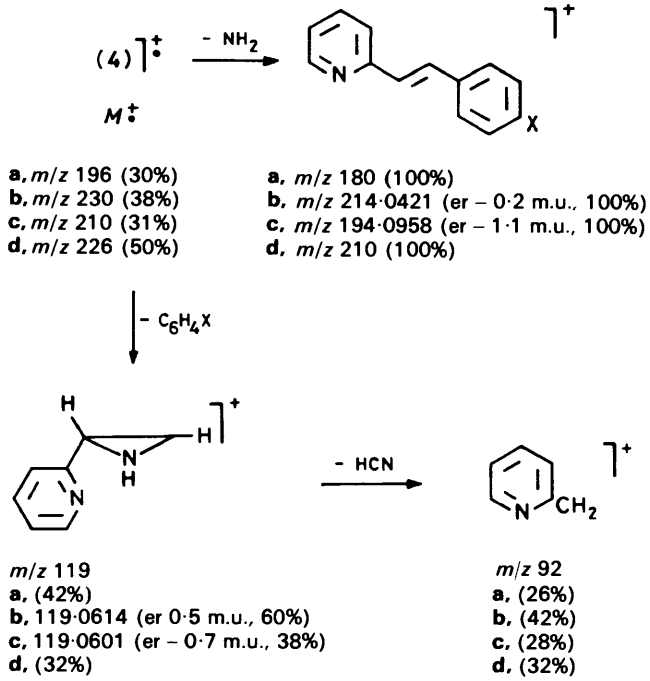
* In the case of aziridine itself where no intramolecular hydrogen bonding is possible, only one band for N–H stretching is observed, at 3 346 cm^{-1} in the vapour phase or at 3 243 cm^{-1} (intermolecular hydrogen-bonding) in the liquid phase (R. W. Mitchell, J. C. Burr, and J. A. Merritt, *Spectrochim. Acta, Part A*, 1967, **23**, 195). Furthermore, the liquid-phase i.r. spectrum of diethyl aziridin-2-ylphosphonate shows two N–H stretching frequences, at 3 450 and 3 420 cm^{-1}, and the latter band is assigned to the intramolecular hydrogen-bonded vibration (S. Rengaraju and K. D. Berlin, *J. Org. Chem.*, 1972, **37**, 3304).

At room temperature, the ^{1}H n.m.r. spectrum of the aziridine (**4a**) consists of signals for two aziridine-ring protons (δ 3.2 and 2.99) and the NH proton of the aziridine ring (broad signal, δ 2.46), together with a strong singlet-like phenyl signal complicated by the ABCD system for 2-pyridyl protons. The broad NH signal disappeared when deuterium oxide was added to the solution. This spectrum is different from that of the *cis* isomer of compound (**4a**), which has been reported to show a singlet at δ 3.7 for the aziridine-ring protons and a singlet at δ 1.92 for the NH proton.[17] In addition, the ^{1}H n.m.r. signals for the two aziridine-ring protons of compound (**4a**) first broadened with decreasing temperature and ultimately split into AB quartets as reported in our preliminary communication.[1] This temperature dependence is explained by an equilibrium for inversion of the imino nitrogen between structures (**9**) and (**10**) (Scheme 2).



Scheme 2.

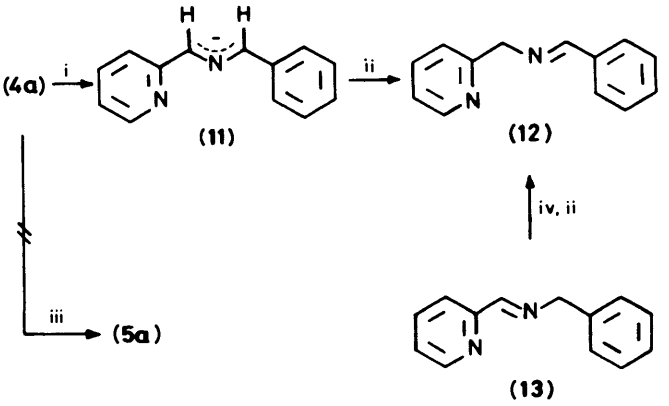
On the other hand, the i.r. spectrum of the enamines (**5a**) suggested the presence of the enamine system (ν_{NH} 3 440, 3 340; $\nu_{C=C}$ 1 625; $\nu_{=CH}$ 790 cm^{-1}), and the ^{1}H n.m.r. spectrum showed a singlet at δ 5.22 for the alkenyl proton, and a broad singlet at δ 5.7 for the amino protons, which disappeared by addition of deuterium oxide, and no aziridine-ring proton was found. A multiplet at δ 7.0 for phenyl protons, and $\nu_{C=C}$ at 1 625 cm^{-1}, suggest the *Z* form. Moreover, the mass spectra of enamines (**5**) are markedly different from those of the aziridines (**4**). For example, the mass spectrum of each enamine (**5**) shows an intense (M − 1) ion peak as a base peak, and all other peaks,



Scheme 3.

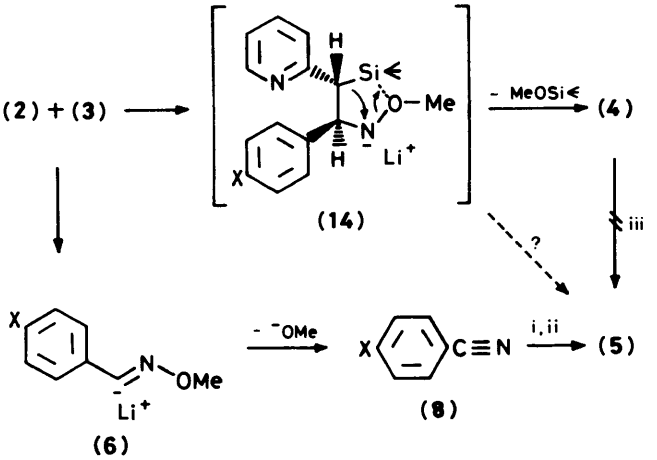
except the molecular ion M^+ peak, are very weak (<18%). On the other hand, the base peak of the spectra of compounds (**4**) results from loss of NH_2 from M^+ ion. The fragmentation and the accurate mass determined are shown in Scheme 3.

On treatment with a large excess of LDA in THF at between −85 and −90 °C, aziridine (**4a**) was not transformed into enamine (**5a**),* but instead was quantitatively transformed into benzylidene-2-picolylamine (**12**) *via cis*-1-phenyl-3-(2-pyridyl)-2-aza-allyl carbanion intermediate (**11**), as shown in Scheme 4.[18] The structure of compound (**12**) was confirmed by a comparison of spectral data with those of a sample prepared independently from compound (**13**) by a base-induced isomerization (Scheme 4).



Scheme 4. *Reagents and conditions:* i, LDA, THF, −85 to −90 °C; ii, water; iii, LDA, THF; iv, LDA

In conclusion, the α-silyl carbanion (**2**) reacts with oxime ethers (**3**) to give the aziridines (**4**) by the elimination of methyl trimethylsilyl ether from an adduct (**14**) (Scheme 5). Although we have proposed in our preliminary communication[1] that the enamine (**5**) may be formed from the intermediate (**14**) as a result of a 1,2-shift of hydride ion from C to N, the new mechanism, involving formation of benzonitrile (**8**) shown in Scheme 5, is more likely than the hydride-shift mechanism. This is because the hydrogen attached to the methoxyimino carbon



Scheme 5. *Reagents:* i, (**2**); ii, ⁻OMe; iii, LDA, THF

* It has been reported that the aziridine ring of ethyl 1,3-diphenylaziridine-2-carboxylate opens to yield ethyl β-anilinocinnamate in the presence of a base (A. J. Speziale, C. C. Tung, K. W. Ratts, and A. Yao, *J. Am. Chem. Soc.*, 1965, **87**, 3460).

of compound (3) should be easily eliminated with anion (2) (or LDA), which are present in large excess at the beginning of the addition of compound (3) to the THF solution of anion (2) (method A). In fact, the hydrogen was easily eliminated from compounds (3) with LDA as mentioned above (Scheme 1); and the formation of enamine (5a) was accelerated by addition of excess of LDA (Table 1). The carbanion (6) thus formed eliminates methoxide ion to yield a benzonitrile (8), which reacts immediately with anion (2) to give enamine (5)[10] after elimination of the trimethylsilyl group from the intermediate *N*-silyl enamine. Moreover, there are two other results to support this new mechanism. The first is that ketoxime (acetophenone or benzophenone oxime) *O*-methyl ethers do not produce the corresponding enamines,[1] and the second is the fact that the formation of enamines (5) is greatly suppressed by the reverse addition of the reactants (method B). The latter evidence is interpreted as follows: this new mechanism which involves the formation of benzonitriles (8) requires two equivalents of anion (2) in order to generate the enamines (5). Therefore, method B is unfavourable for the formation of compound (5), but method A is preferred. In method A, a large excess of the base (2) remains in the reaction mixture at the beginning of the addition of substrate (3), but anion (2) is always deficient in method B. However, these are not always requisite and sufficient conditions for us to eliminate the possibility of the hydride-shift mechanism.

Some of the aziridines (4) were mutagenic for *Salmonella typhimurium* TA 100.[19] Details will be reported elsewhere.

Experimental

All m.p.s (Mitamura micro-melting point apparatus) and b.p.s are uncorrected. U.v. spectra were recorded on a JASCO UVIDEC-505 spectrophotometer for solutions in EtOH, and i.r. spectra were taken on a Hitachi Model 260-50 spectrophotometer. ^{1}H N.m.r. spectra were determined with a JEOL PMX-60SI or JNM FX-90Q spectrometer for solutions in $CDCl_3$ or CCl_4. Chemical shifts are reported in δ-values (internal standard Me_4Si). Mass spectra were recorded with a Hitachi RMU-7M double-focussing mass spectrometer at 70 eV. Elemental analyses were performed at the Institute of Physical and Chemical Research.

Materials.—2-(Trimethylsilylmethyl)pyridine (1) was prepared by a method reported previously,[11] and benzaldehyde oxime *O*-methyl ethers (3a—e) were prepared from the corresponding benzaldehydes and *O*-methylhydroxyl amine hydrochloride in EtOH in the presence of sodium acetate. Yields and m.p. (or b.p.) of (3a), (3b), (3c), (3d), and (3e) were: 48%, b.p. 101 °C/32.5 mmHg (lit.,[20] 86—87 °C/21 mmHg); 91%, m.p. 28 °C, b.p. 92.9 °C/4 mmHg (lit.,[20] b.p. 92—94 °C/4 mmHg); 90%, b.p. 105.7—106.2 °C/17.5 mmHg (lit.,[20] 80—83 °C/5 mmHg); 92%, b.p. 143.2—144.0 °C/24.5 mmHg (lit.,[20] 137—139 °C/22 mmHg); 91%, m.p. 68—69.5 °C (lit.,[21] 69 °C), respectively.

Preparation of trans-2-*Aryl*-3-(2-*pyridyl*)*aziridines* (4a—e) *and* (Z)-1-*Amino*-1-*aryl*-2-(2-*pyridyl*)*ethenes* (5a—d).—The reaction was performed by the following three methods, A, B, and C. The reaction mixture was analysed by ^{1}H n.m.r. spectroscopy before isolation of the products.

Method A. A solution of butyl-lithium in hexane (8.6 g, 0.02 mol) was added to a stirred solution of di-isopropylamine (2.0 g, 0.02 mol) in THF (54 ml) at between −80 and −90 °C under oxygen-free dry nitrogen. To this solution was slowly added the pyridylsilane (1) (3.3 g, 0.02 mol) and the mixture was stirred for an additional 10 min. Then, the mixture was treated with a THF (20 ml) solution of the *O*-methyl oxime (3) (0.02 mol) under the conditions shown in Table 1. The reaction mixture was quenched with water (60 ml) at room temperature and extracted with ether. The crude products thus obtained were analysed by ^{1}H n.m.r. spectroscopy with benzyl alcohol as internal standard. (The results for the aziridine (4a) are summarized in Table 1.) The reaction mixture was concentrated to dryness and the residue was treated with MeOH to remove the enamine (5), and the methanol-soluble part was purified by column chromatography on Florisil. The products were sequentially eluted with hexane, ether, and EtOH. The second and third fractions afforded the aziridine (4). The crude enamine (5) was recrystallized from EtOH. The yields of compounds (4) and (5) for this method (standard procedure, run 1) were reported in our preliminary communciation.[1]

Compound (4a): m.p. 61.4—62.2 °C; $\lambda_{max.}$ 232 (ε 15 900) and 262 nm (7 500); $\nu_{max.}$(KBr) 3 230 (NH), 1 210 (ν_s of aziridine-ring CH), and 855 (ν_{as} of aziridine-ring CH) cm^{-1}; *m/z* 196 (M^+); δ($CDCl_3$) 2.46 (1 H, br, NH), 2.99 (1 H, s, 2-H), 3.2 (1 H, s, 3-H), 7.3 (5 H, s, Ph), and 7.0—8.6 (4 H, ABCD, 2-PyrH) (Found: C, 79.6; H, 6.1; N, 14.3. $C_{13}H_{12}N_2$ requires C, 79.56; H, 6.16; N, 14.28%).

Compound (4b): m.p. 53.5—55.3 °C; $\lambda_{max.}$ 236 (27 200) and 273 nm (12 300); $\nu_{max.}$(KBr) 3 230, 1 215, and 865 cm^{-1}; *m/z* 230 (M^+); δ(CCl_4) 2.26 (1 H, br, NH), 2.62 (1 H, br, 2-H), 3.0 (1 H, br, 3-H), 7.03 (4 H, s, ArH), and 6.47—8.3 (4 H, ABCD, 2-PyrH) (Found: C, 67.45; H, 4.7; N, 12.1%; M^+, 230.0596. $C_{13}H_{11}ClN_2$ requires C, 67.69; H, 4.81; N, 12.14%; *M*, 230.0610).

Compound (4c): m.p. 52.5 °C; $\lambda_{max.}$ 234 (26 700) and 270 nm (14 500); $\nu_{max.}$(KBr) 3 260, 1 210, and 840 cm^{-1}; *m/z* 210 (M^+); δ($CDCl_3$) 2.23 (1 H, s, Me), 2.7 (1 H, br, NH), 2.83 (1 H, d, *J* 2.4 Hz, 3-H), 3.07 (1 H, d, *J* 2.4 Hz, 2-H), 6.9 (4 H, s, ArH), and 6.7—8.2 (4 H, ABCD, 2-PyrH) (Found: C, 79.8; H, 6.6; N, 12.5%; M^+, 210.1140. $C_{14}H_{14}N_2$ requires C, 79.96; H, 6.71; N, 13.32%; *M*, 210.1155).

Compound (4d): m.p. 45.2—46.5 °C; $\lambda_{max.}$ 237 (16 600) and 274 nm (11 600); $\nu_{max.}$(KBr) 3 230, 1 250, and 820 cm^{-1}; *m/z* 226 (M^+); δ(CCl_4) 2.15 (1 H, br, NH), 2.65 (1 H, s, 2-H), 2.99 (1 H, s, 3-H), 3.57 (3 H, s, OMe), and 6.43—8.1 (8 H, ABCD for 2-PyrH complicated by multiplet for Ph) (Found: C, 74.3; H, 6.2; N, 12.4. $C_{14}H_{14}N_2O$ requires C, 73.93; H, 6.21; N, 12.09%).

Compound (5a): m.p. 50—52 °C; $\nu_{max.}$(KBr) 3 440, 3 340, 1 625, and 790 cm^{-1}; *m/z* 196 (M^+); δ(CCl_4) 5.22 (1 H, s, CH), 6.7 (2 H, br, NH_2), 7.0 (5 H, m, Ph), and 6.3—8.13 (4 H, ABCD, PyrH) (Found: M^+, 196.0980. $C_{13}H_{12}N_2$ requires *M*, 196.0999).

Compound (5b): m.p. 125.0—125.5 °C; $\lambda_{max.}$ 236 (13 000), 267 (8 500), and 355 nm (23 500); $\nu_{max.}$(KBr) 3 500, 3 400, 1 618, and 810 cm^{-1}; *m/z* 230 (M^+); δ($CDCl_3$) 5.4 (1 H, s, CH), 6.7 (2 H, br, NH_2), 7.3—7.45 (4 H, AA′BB′, C_6H_4), and 6.7—8.38 (4 H, ABCD, PyrH) (Found: C, 67.6; H, 4.7; N, 12.1. $C_{13}H_{11}ClN_2$ requires C, 67.69; H, 4.81; N, 12.14%).

Compound (5c): m.p. 94.9—95.5 °C; $\lambda_{max.}$ 237 (11 200) and 355 nm (23 800); $\nu_{max.}$(KBr) 3 420, 1 622, and 805 cm^{-1}; *m/z* 210 (M^+); δ(CCl_4) 2.35 (3 H, s, Me), 5.23 (1 H, s, CH), 6.6 (2 H, s, NH_2), and 6.50—8.29 (8 H, ABCD for PyrH complicated by multiplet for C_6H_4) (Found: C, 79.8; H, 6.8; N, 13.2. $C_{14}H_{14}N_2$ requires C, 79.96; H, 6.71; N, 13.32%).

Compound (5d): m.p. 78—81 °C; $\lambda_{max.}$ 251 (9 000) and 354 nm (21 500); $\nu_{max.}$(KBr) 3 420, 1 610, and 805 cm^{-1}; *m/z* 226 (M^+); δ(CCl_4) 3.63 (3 H, s, OMe), 5.10 (1 H, s, CH), 6.5 (2 H, br, NH_2), and 6.3—8.1 (8 H, ABCD for PyrH complicated by multiplet for C_6H_4) (Found: M^+, 226.1080. $C_{14}H_{14}N_2$ requires *M*, 226.1104).

Method B. To a THF (40 ml) solution of an *O*-methyl oxime (3) (0.02 mol) at −80 °C was slowly added a cold solution of compound (2) (0.02 mol) in THF (40 ml), and the mixture was then stirred for 3 h at −80 °C and for 2 h at room temperature. Finally, the reaction mixture was treated with water, and

purified in the same way as in method A except that the enamine (**5**) was not removed by the addition of MeOH. The results are summarized in Table 2.

Method C. To a cooled (−80 °C) mixture of the silane (**1**) (3.3 g, 0.02 mol) and the *O*-methyl oxime (**3a**) (2.7 g, 0.02 mol) in THF (40 ml) was added a cooled (−80 °C) solution of LDA (0.02 mol) in THF (60 ml) during 12 min, and the mixture was stirred for 3.5 h at −80 °C and for 2 h at room temperature. To this mixture was added water (60 ml), and the mixture was extracted with ether and, after evaporation of ether, the residue was analysed by ^{1}H n.m.r. spectroscopy. Yields (recoveries) of compounds (**4a**), (**5a**), (**7**), (**1**), and (**3a**) were 0, 12, 27, 74, and 12% [based on initial quantity of (**1**) or (**3a**)], respectively. After concentration of the mixture, the residue was treated with ether to give *crystalline amidine* (**7**) which was recrystallized from ethanol–ether (0.72 g), m.p. 219.5—221 °C; *m/z* 204 (M^+); $\nu_{max.}$(KBr) 3 280 (NH) and 1 640 cm^{-1} (C=N); δ($CDCl_3$) 1.4 (12 H, d, *J* 6.4 Hz, Me), 3.9 (2 H, septet, *J* 6.4 Hz, CH), 7.3 (5 H, m, Ph), and 9.3 (br, NH) (Found: M^+, 204.1613. $C_{13}H_{20}N_2$ requires *M*, 204.1624).

Isomerization of the Aziridine (**4a**) *to the Imine* (**12**).—A 15% solution of butyl-lithium (670 mg, 1.6 mmol) in hexane was added to a stirred solution of di-isopropylamine (150 mg, 1.5 mmol) in THF (5 ml) at −90 °C under oxygen-free, dry nitrogen. A solution of the aziridine (**4a**) (50 mg, 0.25 mmol) in THF (2 ml) was injected into the solution. The mixture was stirred for 1 h at −90 °C (deep wine colour) and for 2 h at room temperature. The resulting purple solution was cooled to −40 °C, but the colour did not change. Water (5 ml) was added to this cooled solution, and the mixture was extracted with ether to give, after drying (Na_2SO_4) and work-up, an oily product in quantitative yield. The product proved to be identical with an authentic sample of compound (**12**), and none of the enamine (**5a**) was found in the reaction mixture (h.p.l.c.). Compound (**12**) had $\nu_{max.}$(neat) 1 640 cm^{-1} (C=N); δ(CCl_4) 4.73 (2 H, s, CH_2), 8.13 (1 H, s, CH=N), and 8.73—6.7 (10 H, ABCD spin system for 2-pyridyl protons, complicated by phenyl protons).

Preparation of Enamine (**12**).—The Schiff's base (**13**), prepared from pyridine-2-carbaldehyde and benzylamine[22] (yield 83%, b.p. 132 °C/1.5 mmHg; lit.,[23] 165—160 °C/5 mmHg), was isomerized to compound (**12**) in the presence of LDA at −85 °C.[24] The reaction mixture consisted of compound (**12**) and the unchanged Schiff's base (**13**) (30:1, by ^{1}H n.m.r.). Spectral data are shown above.

Reaction of O*-Methyl Oxime* (**3a**) *with LDA; Formation of Benzonitrile* (**8a**).—A THF solution of compound (**3a**) (2.7 g, 0.02 mol) was treated with LDA (0.019 mol) at −80 °C to afford benzonitrile (**8a**) in 67% yield (details will be reported separately).[14]

Addition of LDA to Benzonitrile (**8a**); *Formation of Amidine* (**7**).—To a THF (25 ml) solution of LDA (0.02 mol) at −85 °C was added benzonitrile (**8a**) (2.10 g, 0.02 mol). After being stirred for 1 h at −85 °C, the mixture was treated with aqueous THF (20 ml) and then with water (60 ml). An ethereal extract gave, after work-up *N'*,*N'*-di-isopropylbenzamidine (**7**) in 73% yield (^{1}H n.m.r.), m.p. 219.5—221 °C. Spectral data are shown above.

Elimination of Trimethylsilyl Group from (Z)-β-(2-*pyridyl*)-α-(*trimethylsilylamino*)*styrene*; *Formation of Enamine* (**5a**).—To a THF (30 ml) solution of the *N*-silyl enamine (0.01 mol) prepared from anion (**2**) and benzonitrile (**8a**),[10] was added a solution of lithium methoxide (0.01 mol) in MeOH (5 ml). After being stirred for 2 h at room temperature, the reaction mixture was treated with water (60 ml). Extraction (ether) and work-up gave compound (**5a**) in 92% yield (^{1}H n.m.r.), with m.p. (50—52 °C), i.r., and ^{1}H n.m.r. spectra identified with those of compound (**5a**) obtained by method A.

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