Triazolines. XXXIII. Nonregiospecific 1,3-Cycloaddition of Aryl Azides to Vinylpyridines: A Unique Route to the Synthesis of 2-Pyridyl Substituted Aziridines *via* Unstable 4-Pyridyltriazoline Intermediates

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The 1,3-cycloaddition of aryl azides to the olefinic bonds of 4- and 2-vinylpyridines has been found to yield pyridyl substituted aziridines as the main reaction products with only smaller amounts of the normally expected 1-aryl-5-pyridyl-1,2,3-triazolines. Theoretical and experimental evidence are provided to explain the results: based on the fact that the olefinic bonds in 4- and 2-vinylpyridines are electron-deficient, azide addition can be expected to be not regiospecific. In the bidirectional addition reaction, the $HOMO_{azide}$-$LUMO_{olefin}$ interaction predominates leading to unstable 1-aryl-4-pyridyl-1,2,3-triazolines, which, unlike the more stable 5-pyridyl compounds, lose nitrogen under thermal conditions to yield the aziridines. At room temperature, the reactions yield the aziridine along with the 1-aryl-4-pyridyltriazole, providing evidence for the formation of the 4-pyridyltriazoline intermediate. Reaction of the vinylpyridines with variously substituted phenyl azides, clearly indicates that the electron donating methyl and methoxy groups on the phenyl azide facilitate reaction, while the electron withdrawing nitro group has a retarding effect. This is consistent with an increase in the $HOMO_{azide}$ energy and hence in azide reactivity. According to the FMO model, the 1,3-cycloaddition of aryl azides to vinylpyridines appears to be predominantly, but not exclusively, a $HOMO_{azide}$-$LUMO_{olefin}$ interaction and provides a unique route to the synthesis of 2-pyridyl substituted aziridines.

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Introduction.

During the past several years, we have been interested in the synthesis and pharmacological evaluation of different heterocyclic substituted 1,2,3-triazolines and aziridines. In particular, the 1-aryl-5-pyridyl-1,2,3-triazolines display significant anticonvulsant activity [1,2,3,4] and the aziridines, well known for their pharmacological significance in the past [5], also appear to have similar potential as anticonvulsant agents [4].

Although there are efficient methods for the synthesis of alkyl and aryl substituted aziridines [6-8], few heterocyclic substituted aziridines are known. One attractive method for the synthesis of aryl substituted aziridines involves ring contraction of the five-membered 1,2,3-triazoline heterocycles through nitrogen extrusion under photochemical conditions. This method, however, when applied to the preparation of pyridyl substituted aziridines using 1-aryl-5-pyridyltriazolines, yields a mixture of products from which the pure aziridine is obtained only in very low yields [4].

In the course of preliminary investigations on the cycloaddition of aryl azides to 4-vinylpyridine in refluxing benzene, as a safer approach to the scaled up synthesis of 1-aryl-5-pyridyl-1,2,3-triazolines that does not involve the reaction of large amounts of the hazardous diazomethane with aldimines [1,4], we found that pyridyl substituted aziridines were formed as the major products, with the 1,5-substituted triazolines only in minor amounts [9]. Fractional crystallization along with chromatographic methods were used to separate the aziridines from the triazolines in the reaction mixture. The final results indicated that these reactions, when compared to triazoline photolysis are relatively cleaner and give better yields of aziridines with no detectable formation of ketimine side products. This has prompted us to investigate in detail the reaction of several substituted phenyl azides with both 4- and 2-vinylpyridines, with the objective to study substituent effects and to elucidate a possible reaction path for aziridine formation.

Results and Discussion.

The Frontier Molecular Orbital (FMO) treatment of 1,3-cycloadditions permits a rational interpretation of the effect of substituents on reactivity and regioselectivity. Reactions fall into three types, depending on whether the dominant interaction is between the highest occupied molecular orbital (HOMO) of the dipole and the lowest unoccupied molecular orbital (LUMO) of the dipolarophile, or the dipole LUMO and the dipolarophile HOMO, or whether both interactions are of comparable significance [10-12]. In the case of azide addition to electron rich olefins, the dominant interaction will be $HOMO_{olefin}$-$LUMO_{azide}$, whereas $HOMO_{azide}$-$LUMO_{olefin}$ interaction will govern additions to electron poor olefins. While HOMO energy is increased by electron donating groups, LUMO energy is decreased by electron withdrawing substituents [7,10-12].

In general, the 1,3-cycloaddition reactions of organic azides with olefinic carbon-carbon double bonds are considered concerted, stereospecific, *cis* additions, with the

terminal azido nitrogen attacking the more nucleophilic olefinic carbon [13]. Unsymmetrically substituted olefins also exhibit a marked orientational specificity, the direction of addition being controlled by electronic rather than steric factors. Thus, they give only one triazoline isomer, as in the case of phenyl azide-styrene adducts, which are exclusively, 1,5-diphenyltriazolines [14,15]. The same rules for orientational specificity apply to electron-rich olefins (*eg.* enamines) and olefins bearing electron-withdrawing groups (*eg.* methyl acrylate). As a rule, azide addition to electron-rich enamines is $LUMO_{azide}$ controlled, since the larger terminal coefficient is on the unsubstituted nitrogen of the azide and the unsubstituted terminus in the dipolarophile, and the electron releasing groups appear at the 5-position of the triazoline ring. In contrast, the reactions of organic azides with electron-deficient dipolarophiles are $HOMO_{azide}$ controlled; union of the substituted azide nitrogen with the unsubstituted dipolarophile carbon, leads to the electron withdrawing substituents at the 4-position. However, azide addition to electron deficient olefinic bonds is not always regiospecific. In most instances, where two isomers are possible, one isomer usually predominates, often to the exclusion of the other [16].

The olefinic bond in 4-vinylpyridine can be considered to be an electron-deficient one, since it is conjugated with the electron-deficient pyridine ring. Pyridine, quinoline and similar heterocyclic ring systems, where the nitrogen is incorporated onto the six-membered ring, are considered electronwithdrawing or π-deficient as opposed to pyrroles, *etc.*, which are π-excessive [17,18]. Thus, according to the FMO model, azide addition to vinylpyridine can be anticipated to be $HOMO_{azide}$ controlled and hence should give the 4-pyridyl-Δ^2-1,2,3-triazoline as the expected product. However, the reaction yields two products, a 1-aryl-2-pyridylaziridine as the major product, and a 1-aryl-5-pyridyltriazoline as a minor product, but in noticeable amounts. It is proposed that the cycloaddition reaction leads to two isomeric triazolines from a bidirectional addition, with the predicted 1-aryl-4-(4-pyridyl)-1,2,3-triazoline predominating, but as an unstable intermediate that decomposes with loss of nitrogen to yield the aziridine, whereas the isomeric 5-pyridyltriazoline is stable at the reaction temperature and undergoes no decomposition. Apparently, azide addition to 4-vinylpyridine is not governed exclusively by the $HOMO_{azide}$-$LUMO_{olefin}$ interaction mode, but rather, the $HOMO_{olefin}$-$LUMO_{azide}$ interaction also exists, with the former mode predominating. In contrast, the 1,3-cycloaddition of azides to olefins bearing simple electron-withdrawing groups, such as the addition of phenyl azide to methyl acrylate, is highly regioselective and leads exclusively to 1,4-disubstituted triazolines [7,19,20].

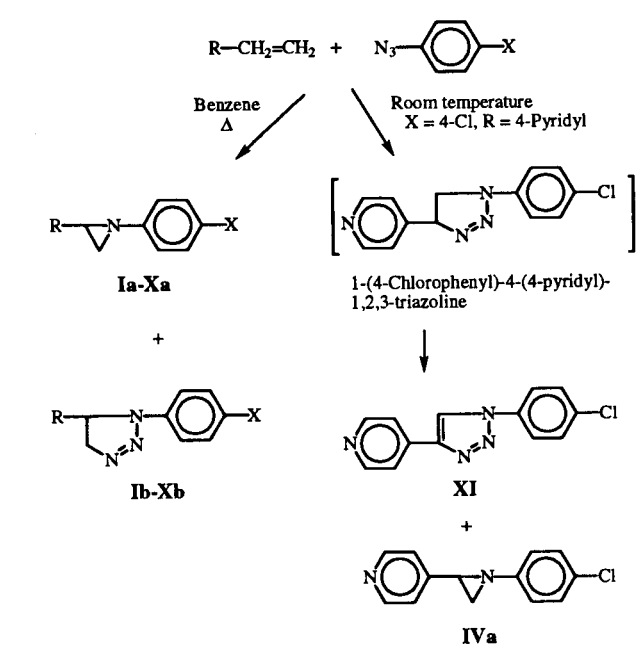
Experimental evidence has been obtained to support the proposed bidirectional reaction path and the formation of the 1,4-substitued triazoline intermediate that leads to the aziridine (see Scheme). Since the FMO theory predicts that the 4-pyridyl substituted triazolines are the most probable products resulting from the cycloaddition, the aziridines are apparently formed through the *in situ* thermal decomposition of these 4-pyridyltriazoline intermediates produced during the cycloaddition at the reflux temperature of benzene (~80°); the 5-pyridyltriazolines are stable at this temperature and remain intact in the reaction mixture. Even if the 5-pyridyl compounds were to undergo thermal decomposition, they would produce ketimines [21] and not aziridines, which are formed only by photolysis of these triazolines [8,22]. Evidence for the formation of the 4-pyridyltriazoline intermediates is also obtained from the addition reaction of 4-chlorophenyl azide to 4-vinylpyridine, conducted at room temperature, when 4-pyridyltriazole **XI** and the aziridine **IVa** are obtained as the sole reaction products. The 4-pyridyl substituted triazole **XI** provides key evidence that the corresponding 4-pyridyl substituted triazoline must be the intermediate in the cycloaddition reaction, because **XI** can result only from dehydrogenation of the 4-pyridyltriazoline and it is distinctly different from the 5-pyridyltriazole formed by oxidation of the corresponding 5-pyridyltriazoline **IVb** [23].

Apparently, the 4-pyridyl substituted triazolines, unlike the 5-pyridyl compounds, are very unstable; at room temperature they undergo part aromatization to the stable triazoles and part ring contraction to the aziridines, but when heated, complete *in situ* thermolysis occurs to yield exclusively, the aziridines. This is consistent with previous observations that triazolines bearing an electron withdrawing group in the 4-position tend to undergo thermolysis with nitrogen expulsion to give aziridines [7,19,24]. Obviously, olefin-azide addition is not the reaction of choice for the preparation of 1-aryl-5-pyridyl-1,2,3-triazolines, as opposed to the diazomethane-imine reaction, where the 1,5-substituted triazolines, both aryl and heteroaryl, are formed exclusively in large yields [7,15,25,26].

In our investigations, a variety of 4-substituted phenyl azides has been reacted with both 4-vinyl- and 2-vinylpyridines, as well as 4-nitrostyrene, with a view to obtain additional support that the cycloaddition is indeed controlled by the HOMO energy of the azide. The general procedure was to vigorously reflux the mixture of the azide and the vinylpyridine in benzene for a period of 16-24 hours, the length of reflux depending on the reactivity of the azide. The less reactive azides required longer reaction times, particularly, the nitrophenyl azide which required 48 hours of reflux.

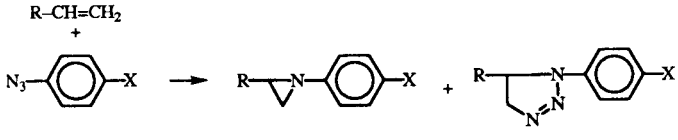
Proton nmr spectroscopy is used to analyze the composition of the crude product mixture, particularly to determine the ratio of the aziridine to the triazoline in each reaction. Both compounds have characteristic well-separated chemical shift patterns for the $-CH_2$ and -CH protons, the aziridine protons appearing upfield and those of the triazoline,

Scheme



Table

Summary of Reactions and Product Yields from the 1,3-Cycloaddition of Substituted Phenyl Azides to 4-Vinyl- and 2-Vinylpyridines



Compound Numbers	X	Reaction Time, hours	Yield, %	
			Aziridines	Triazolines
R= 4-Pyridyl			**Ia-VIa**	**Ib-VIb**
Ia, Ib	CH_3O-	24	50	20
IIa, IIb	CH_3-	16	53	21
IIIa, IIIb	H-	16	40	26
IVa, IVb	Cl-	16	49	10
Va, Vb	CF_3-	16	32	15
VIa, VIb	NO_2-	48	22	12
R= 2-Pyridyl			**VIIa-IXa**	**VIIb-IXb**
VIIa, VIIb	CH_3O-	24	45	22 [a]
VIIIa, VIIIb	Cl-	16	46	15 [a]
IXa, IXb	H-	16	41	22 [a]
R= 4-Nitrophenyl			**Xa**	**Xb**
Xa, Xb	Cl-	36	25	13

[a] The triazoline **VIIb, VIIIb,** and **IXb** yields for the 2-pyridyl series were estimated by ^{1}H nmr analysis; see text for details.

downfield. The -CH_2 and -CH protons of the aziridine show two sets of a doublet of a doublet around 2.5 ppm, and a single doublet of a doublet around 3.1 ppm respectively. The -CH protons of the corresponding triazoline appear as a quartet in the 4.3 ppm region while the -CH_2 protons give two overlapped quartets around 4.9 ppm. Most of the 1,5-substituted triazolines obtained from these reactions have been reported previously from our labs [26] and the ^{1}H nmr spectroscopic data and melting points of the products obtained here are well consistent with the reported data. The triazolines have been further identified in this work by ^{13}C nmr.

The analysis of the crude reaction products, in general, indicated that the ratio of the aziridine to the triazoline was in the range of 1.5:1 to 5:1; thus in all the reactions conducted, the aziridine was the major product and the triazoline, the minor. The yields of pure aziridines **Ia-VIa** and **VIIa-IXa** obtained from the reactions of phenyl azides with 4-vinyl- and 2-vinylpyridines as also **Xa** from the reaction with 4-nitrostyrene, are given in the Table. The results clearly point out that the electron releasing methyl and methoxy groups on the phenyl azide facilitate addition, with the highest yields for aziridines, **Ia** and **IIa**, while the electron withdrawing nitro group on the phenyl azide retards reaction with the lowest yield for **VIa**. An electron-donating group on the phenyl azide would increase the energy of its HOMO orbitals and lead to a decrease in the energy gap between the $HOMO_{azide}$ and $LUMO_{olefin}$, and therefore increase the reactivity. Thus all of the theoretical and experimental evidence for the vinylpyridine-azide addition are consistent with a $HOMO_{azide}$ -$LUMO_{olefin}$ interaction as the predominating mode, though not exclusive. In fact, the magnitude of the actual yields of the aziridines which reflects the reactivity of the phenyl azides, is also largely consistent with the electron-donating ability of the substituents to enhance azide reactivity, the order being, -CH_3>-OCH_3>-Cl>H>-CF_3 >-NO_2. Thus, the experimental results support that the reaction is $HOMO_{azide}$ controlled, the lesser the electron-releasing effect of the azide substituent group, the lesser the reactivity of the 1,3-cycloaddition reaction.

In reacting phenyl azides with both 4- and 2-vinylpyridines, it was of interest to see if the 4-vinylpyridine, with its more extended conjugation with the vinyl group, would increase aziridine formation compared to the 2-vinylpyridine. However, the yields of **IIIa** and **IXa** and **IVa** and **VIIIa** are quite comparable and show no significant difference as expected. Similarly, it is remarkable that the electron withdrawing effect of the nitrophenyl group in 4-nitrostyrene is not as strong as it should be; the aziridine **Xa** is formed to a much lesser extent compared to **IVa** and **VIIIa**.

In conclusion, the reaction of phenyl azides with vinylpyridines under thermal conditions affords a unique route to the synthesis of pyridyl substituted aziridines. The reactions are relatively clean and the yields are acceptable. According to the FMO model, the 1,3-cycloaddition of aryl azides to vinylpyridines appears to be predominantly,

but not exclusively, a $HOMO_{azide}$-$LUMO_{olefin}$ interaction, as evidenced by the preferential formation of the 1-phenyl-4-pyridyltriazoline which at reflux decomposes *in situ* to give exclusively the aziridines and at room temperature, a mixture of the 4-pyridyltriazole and aziridine.

EXPERIMENTAL

Melting points were taken in a Thomas-Hoover capillary melting point apparatus and are uncorrected. The ^1H (300 MHz) and ^{13}C (75 MHz) nmr spectra were determined with a Varian VXR-300S FT spectrometer using deuteriochloroform solutions with tetramethylsilane as the internal standard. Elemental analyses were performed by Oneida Research Services, Inc., One Halsey Road, Whitesboro, NY 13492. Mass spectra were recorded on a Kratos-Concept spectrometer under the fast atom bombardment mode or the electron impact mode as the case may be. Column chromatography was carried out on silica gel (70-230 mesh) purchased from Aldrich Chemicals. Vinylpyridines and 4-nitrostyrene were also purchased from Aldrich Chemicals and used as supplied. The phenyl azides were prepared according to literature procedure [27] from the corresponding anilines, *via* reaction of the diazonium salts with sodium azide.

General Procedure for the Reaction of Phenyl Azides with Vinylpyridines and 4-Nitrostyrene.

The aryl azide (0.02 mole) was added to a solution of an equimolar amount of vinylpyridine in benzene (50 ml). The mixture was refluxed with magnetic stirring for 16-24 hours. The resulting reddish brown reaction mixture was subjected to rotary evaporation under reduced pressure, when a brown oily residue was obtained.

In the case of 4-vinylpyridine reactions for the preparation of compounds **I-VI**, the residue was treated with methyl *tert*-butyl ether (~ 20 ml), and allowed to cool in a refrigerator for approximately 12 hours, whereupon the majority of the triazoline products **Ib-VIb** precipitated. The crude triazolines were filtered and recrystallized from appropriate solvents (see Table). The filtrates containing the aziridines **Ia-VIa** were concentrated and the oily residues subjected to column chromatographic purification to yield the pure aziridines (Table). The residues were dissolved in the minimum amount of methylene chloride and the solutions chromatographed through a silica gel column. The column was eluted first with chloroform and then with a mixture of ethyl acetate and chloroform (v/v = 1:1), yielding three major fractions. The first fraction contained all the unreacted azide and vinylpyridine. The aziridines were present in the second fraction, and the triazolines (any still remaining after the initial precipitation), in the third. After removal of the solvents *in vacuo* from the aziridine fraction, an oily product remained which solidified to yield the aziridines in most cases, except the 1-(4-trifluoromethylphenyl)-2-(4-pyridyl)aziridine (**Va**), which was an oil. The chromatographic separation was monitored by analytical thin layer chromatography on Merck precoated plates and the products were visualized by uv light.

The brown oily residues obtained from the reactions of aryl azides with 2-vinylpyridine **VII-IX**, were analyzed directly by ^1H nmr and an estimate of the amount of triazolines **VIIb-IXb** formed in the reactions obtained; no attempts were made to isolate **VIIb-IXb** due to their unstable nature (Table). The oily residues were then subjected to column chromatographic separation to afford the pure aziridines **VIIa-IXa**, using the same approach as that described above for the 4-vinylpyridine reactions. The 1-(4-methoxyphenyl)-2-(2-pyridyl)aziridine (**VIIa**) and 1-phenyl-2-(2-pyridyl)aziridine (**IXa**) are both oils (Table). The products **Xa** and **Xb** from the reaction of 4-chlorophenyl azide with 4-nitrostyrene were isolated in the same manner as those from the 4-vinylpyridine reactions.

1-(4-Methoxyphenyl)-2-(4-pyridyl)aziridine (**Ia**).

This compound was obtained as a white crystalline solid, mp 52-54°; ^1H nmr: δ 2.35 (dd, 3-CH_2, J_1 = 3.3 Hz, J_2 = 0.9 Hz, 1 H), 2.48 (dd, 3-CH_2, J_1 = 6.6 Hz, J_2 = 0.9 Hz, 1 H), 2.98 (dd, 2-CH, J_1 = 6.6 Hz, J_2 = 3.3 Hz, 1 H) [**Ib**: 4.22 (m, 5-CH, 1H), 4.84 (m, 4-CH_2, 2 H)] [26], 3.77 (s, OCH_3, 3H), 6.81 (dt, J_1 = 9.0 Hz, J_2 = 2.1 Hz, 2 H), 6.95 (dt, J_1 = 8.7 Hz, J_2 = 2.1 Hz, 2 H), 7.29 (dd, J_1 = 4.8 Hz, J_2 = 1.5 Hz, 2 H), 8.56 (dd, J_1 = 4.8 Hz, J_2 = 1.5 Hz, 2 H); ^{13}C nmr: δ 38.3 (CH_3O), 40.6 (CH_2), 55.5 (CH), 114.4 (Ph C), 121.2 (Ph C), 121.3 (Pyr C), 146.9 (Ph C), 148.8 (Pyr C), 149.8 (Pyr C), 155.5 (Ph C).

Anal. Calcd. for $C_{14}H_{14}N_2O$: C, 74.31; H, 6.24; N, 12.38. Found: C, 74.25; H, 6.31; N, 12.36.

Triazoline **Ib** was obtained as a beige solid, mp 147-149° dec (lit [26] 143-145°); ^{13}C nmr: δ 55.5 (CH_3O), 57.9 (CH_2), 74.8 (CH), 114.6 (Ph C), 116.5 (Ph C), 121.1 (Pyr C), 133.8 (Ph C), 149.3 (Pyr C), 150.7 (Pyr C), 155.7 (Ph C).

1-(4-Methylphenyl)-2-(4-pyridyl)aziridine (**IIa**).

This compound was obtained as a white crystalline solid, mp 123-125°; ^1H nmr: δ 2.29 (s, CH_3, 3 H), 2.36 (dd, 3-CH_2, J_1 = 3.3 Hz, J_2 = 1.2 Hz, 1 H), 2.49 (dd, 3-CH_2, J_1 = 6.6 Hz, J_2 = 1.2 Hz, 1 H), 3.01 (dd, 2-CH, J_1 = 6.6 Hz, J_2 = 3.3 Hz, 1 H) [**IIb**: 4.24 (m, 5-CH, 1 H), 4.85 (m, 4-CH_2, 2 H)] [26], 6.92 (dt, J_1 = 8.5 Hz, J_2 = 2.1 Hz, 2 H), 7.07 (dt, J_1 = 8.7 Hz, J_2 = 2.1 Hz, 2 H), 7.30 (dd, J_1 = 4.8 Hz, J_2 = 1.5 Hz, 2 H), 8.57 (dd, J_1 = 4.5 Hz, J_2 = 1.8 Hz, 2 H); ^{13}C nmr: δ 20.7 (CH_3), 38.1 (CH_2), 40.4 (CH), 120.3 (Ph C), 121.3 (Ph C), 129.7 (Pyr C), 132.4 (Ph C), 148.8 (Ph C), 149.8 (Pyr C), 151.2 (Pyr C).

Anal. Calcd. for $C_{14}H_{14}N_2$: C, 79.97; H, 6.71; N, 13.32. Found: C, 79.67; H, 6.78; N, 13.32.

Triazoline **IIb** was obtained as a beige solid, mp 154-156° dec (lit [26] 157-158°); ^{13}C nmr: δ 20.6 (CH_3), 57.3 (CH_2), 74.8 (CH), 114.9 (Ph C), 121.0 (Ph C), 129.9 (Pyr C), 132.5 (Ph C), 137.6 (Ph C), 149.3 (Pyr C), 150.7 (Pyr C).

1-Phenyl-2-(4-pyridyl)aziridine (**IIIa**).

This was obtained as a white crystalline solid, mp 48-50°; ^1H nmr: δ 2.39 (dd, 3-CH_2, J_1 = 3.3 Hz, J_2 = 1.2 Hz, 1 H), 2.54 (dd, 3-CH_2, J_1 = 6.6 Hz, J_2 = 1.2 Hz, 1 H), 3.07 (dd, 2-CH, J_1 = 6.6 Hz, J_2 = 3.3 Hz, 1 H) [**IIIb**: 4.25 (m, 5-CH, 1 H), 4.85 (m, 4-CH_2, 2H)] [26], 7.02 (m, 3 H), 7.26 (dm, J = 7.5 Hz, 2 H), 7.31 (dd, J_1 = 4.5 Hz, J_2 = 1.5 Hz, 2 H), 8.57 (dd, J_1 = 4.6 Hz, J_2 = 1.5 Hz, 2 H); ^{13}C nmr: δ 38.0 (CH_2), 40.3 (CH), 120.4 (Ph C), 121.3 (Ph C), 123.0 (Ph C), 129.2 (Pyr C), 148.7 (Ph C), 149.9 (Pyr C), 153.6 (Pyr C).

Anal. Calcd. for $C_{13}H_{12}N_2$: C, 79.56; H, 6.16; N, 14.27. Found: C, 79.29; H, 6.19; N, 14.20.

Triazoline **IIIb** crystallized as a white solid, mp 157-159° dec (lit [26] 160-161°); ^{13}C nmr: δ 56.9 (CH_2), 75.0 (CH), 114.8 (Ph C), 120.9 (Ph C), 122.9 (Ph C), 129.4 (Pyr C), 140.0 (Ph C), 149.2 (Pyr C), 150.8 (Pyr C).

1-(4-Chlorophenyl)-2-(4-pyridyl)aziridine (**IVa**).

This was obtained as a white crystalline material, mp 105-106°; ^{1}H nmr: δ 2.40 (dd, 3-CH_2, J_1 = 3.3 Hz, J_2 = 1.2 Hz, 1 H), 2.50 (dd, 3-CH_2, J_1 = 6.6 Hz, J_2 = 1.2 Hz, 1 H), 3.04 (dd, 2-CH, J_1 = 6.6 Hz, J_2 = 3.3 Hz, 1 H) [**IVb**: 4.32 (m, 5-CH, 1 H), 4.92 (m, 4-CH_2, 2 H)] [26], 6.95 (dd, J_1 = 6.6 Hz, J_2 = 2.1 Hz, 2 H), 7.22 (dd, J_1 = 6.9 Hz, J_2 = 2.1 Hz, 2 H), 7.29 (dd, J_1 = 4.5 Hz, J_2 = 1.8 Hz, 2 H), 8.58 (dd, J_1 = 4.5 Hz, J_2 = 1.8 Hz, 2 H); ^{13}C nmr: δ 38.1 (CH_2), 40.5 (CH), 121.2 (Ph C), 121.7 (Ph C), 128.0 (Ph C), 129.1 (Pyr C), 148.1 (Ph C), 149.9 (Pyr C), 152.2 (Pyr C).

Anal. Calcd. for $C_{13}H_{11}N_2Cl$: C, 67.67; H, 4.82; N, 12.15. Found: C, 67.99; H, 4.65; N, 12.43.

Triazoline **IVb** separated as a white crystalline solid, mp 151-153° dec (lit [26] 151-152°); ^{13}C nmr: δ 56.9 (Triazoline C), 75.3 (Triazoline C), 116.0 (Ph C), 120.8 (Ph C), 128.0 (Ph C), 129.4 (Pyr C), 138.5 (Ph C), 148.6 (Pyr C), 150.9 (Pyr C).

1-(4-Trifluoromethylphenyl)-2-(4-pyridyl)aziridine (**Va**).

This compound was obtained as a yellowish oil, bp 126-128°/0.2 mm Hg; ^{1}H nmr: δ 2.46 (dd, 3-CH_2, J_1 = 3.0 Hz, J_2 = 1.2 Hz, 1 H), 2.57 (dd, 3-CH_2, J_1 = 6.6 Hz, J_2 = 1.2 Hz, 1 H), 3.12 (dd, 2-CH, J_1 = 6.6 Hz, J_2 = 3.0 Hz, 1 H) [**Vb**: 4.38 (m, 5-CH, 1 H), 4.96 (m, 4-CH_2, 2 H)] [26], 7.09 (d, J = 8.7 Hz, 2 H), 7.31 (dd, J_1 = 4.5 Hz, J_2 = 1.5 Hz, 2 H), 7.52 (d, J = 8.9 Hz, 2 H), 8.59 (dd, J_1 = 4.5 Hz, J_2 = 1.5 Hz, 2 H); ^{13}C nmr: δ 38.0 (CH_2), 40.4 (CH), 120.6 (Ph C, 4), 121.2 (Pyr C, 2), 126.4 (quartet, CF_3), 147.8 (Ph C, 1), 149.9 (Pyr C, 2), 151.0 (Ph C, 1), 156.7 (Pyr C, 1). ms: (EI) m/z (%) 264 (M^+, 32), 263 [$(M-1)^+$, 54], 245 (21), 145 ($C_6H_4CF_3^+$, 100), 119 (16).

Anal. Calcd. for $C_{14}H_{11}F_3N_2$: C, 63.64; H, 4.20; N, 10.60. Found: C, 63.29; H, 4.21; N, 10.43.

Triazoline **Vb** was obtained as a colorless solid, mp 149-150° dec (lit [1] 149-150°); ^{13}C nmr: δ 56.4 (CH_2), 75.7 (CH), 114.4 (Ph C, 4), 120.7 (Pyr C, 2), 125.9 (Ph C, 1), 126.7 (quartet, CF_3), 142.4 (Ph C, 1), 148.3 (Pyr C, 1), 151.0 (Pyr C, 2).

1-(4-Nitrophenyl)-2-(4-pyridyl)-aziridine (**VIa**).

This was obtained as a yellish white crystalline solid mp 142-143°; ^{1}H nmr : δ 2.54 (dd, 3-CH_2, J_1 = 3.0 Hz, J_2 = 1.2 Hz, 1 H), 2.64 (dd, 3-CH_2, J_1 = 6.6 Hz, J_2 = 1.2 Hz, 1 H), 3.22 (dd, 2-CH, J_1 = 6.6 Hz, J_2 = 3.0 Hz, 1 H) [**VIb**: 4.46 (m, 5-CH, 1 H), 5.01 (m, 4-CH_2, 2 H)] [26], 7.10 (dt, J_1 = 9.0 Hz, J_2 = 1.8 Hz, 2 H), 7.31 (dd, J_1 = 4.5 Hz, J_2 = 1.8 Hz, 2 H), 8.17 (dt, J_1 = 9.0 Hz, J_2 = 1.8 Hz, 2 H), 8.61 (dd, J_1 = 4.5 Hz, J_2 = 1.8 Hz, 2 H); ^{13}C nmr: δ 38.2 (CH_2), 40.6 (CH), 120.6 (Ph C), 121.1 (Ph C), 125.3 (Pyr C), 147.1 (Ph C), 150.1 (Pyr C), 150.6 (Ph C), 159.5 (Pyr C).

Anal. Calcd. for $C_{13}H_{11}N_3O_2$: C, 64.72; H, 4.60; N, 17.42. Found: C, 64.87; H, 4.63; N, 17.42.

Triazoline **VIb**, mp 156-158° dec (lit [23] 151-152°); ^{13}C nmr: δ 56.4 (Triazoline C), 76.7 (Triazoline C), 114.6 (Ph C), 121.0 (Ph C), 126.2 (Pyr C), 143.0 (Ph C), 145.0 (Ph C), 148.2 (Pyr C), 151.6 (Pyr C).

1-(4-Methoxyphenyl)-2-(2-pyridyl)aziridine (**VIIa**).

This was obtained as a yellowish oil, bp 145-148°/0.2 mm Hg; ^{1}H nmr: δ 2.45 (dd, 3-CH_2, J_1 = 6.6 Hz, J_2 = 1.2 Hz, 1 H), 2.53 (dd, 3-CH_2, J_1 = 3.3 Hz, J_2 = 1.2 Hz, 1 H), 3.23 (dd, 2-CH, J_1 = 6.6 Hz, J_2 = 3.3 Hz, 1H) [**VIIb**: 4.40 (q, 5-CH, J_1 = 17.1 Hz, J_2 = 8.40 Hz, 1 H), 4.88 (m, 4-CH_2, 1 H), 5.09 (m, 4-CH_2, 1 H)] [26], 3.76 (s, 3 H), 6.80 (dd, J_1 = 6.6 Hz, J_2 = 2.4 Hz, 2 H), 7.00 (dd, J_1 = 6.6 Hz, J_2 = 2.4 Hz, 2 H), 7.19 (td, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1 H), 7.35 (dt, J_1 = 7.8 Hz, J_2 = 0.9 Hz, 1 H), 7.66 (td, J_1 = 7.8 Hz, J_2 = 1.5 Hz, 1 H), 8.56 (dq, J_1= 4.8 Hz, J_2 = 0.9 Hz, 1 H); ^{13}C nmr: δ 37.3 (CH_3), 42.8 (CH_2), 55.5 (CH), 114.3 (Ph C), 120.3 (Pyr C), 121.4 (Ph C), 122.3 (Pyr C), 136.6 (Pyr C), 147.4 (Ph C), 155.4 (Ph C), 149.2 (Pyr C), 158.9 (Pyr C).

Anal. Calcd. for $C_{14}H_{14}N_2O$: C, 74.31; H, 6.24; N, 12.38. Found: C, 73.89; H, 6.17; N, 12.29.

1-(4-Chlorophenyl)-2-(2-pyridyl)aziridine (**VIIIa**).

This compound was obtained as a white crystalline solid, mp 75-77°; ^{1}H nmr: δ 2.48 (dm, 3-CH_2, J = 6.6 Hz, 1 H), 2.60 (dm, 3-CH_2, J = 3.3 Hz, 1 H), 3.27 (dd, 2-CH, J_1 = 6.6 Hz, J_2 = 3.3 Hz, 1 H) [**VIIIb**: 4.46 (q, 5-CH, J_1 = 17.1 Hz, J_2 = 7.50 Hz, 1 H), 4.92 (m, 4-CH_2, 1H), 5.10 (m, 4-CH_2, 1 H)] [26], 6.99 (dt, J1 = 6.8 Hz, J_2 = 2.4 Hz, 2 H), 7.20 (dd, J_1 = 6.7 Hz, J_2 = 2.1 Hz, 2 H), 7.21 (m, 1 H), 7.35 (dt, J_1 = 7.8 Hz, J_2 = 0.9 Hz, 1 H), 7.69 (td, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1 H), 8.58 (dt, J_1 = 5.1 Hz, J_2 = 0.9 Hz, 1 H); ^{13}C nmr: δ 37.1 (CH_2), 42.7 (CH), 120.4 (Pyr C), 121.9 (Ph C), 122.5 (Pyr C), 127.7 (Ph C), 129.0 (Ph C), 136.7 (Pyr C), 149.4 (Pyr C), 152.7 (Ph C), 158.3 (Pyr C).

Anal. Calcd. for $C_{13}H_{11}N_2Cl$: C, 67.68; H, 4.81; N, 12.14. Found: C, 67.84; H, 4.60; N, 12.25.

1-Phenyl-2-(2-pyridyl)aziridine (**IXa**).

This was obtained as a yellowish oil, bp 108-110°/0.2 mm Hg; ^{1}H nmr: δ 2.50 (dm, 3-CH_2, J = 6.3 Hz, 1 H), 2.57 (dm, 3-CH_2, J = 3.0 Hz, 1 H), 3.31 (dd, 2-CH, J_1 = 6.3 Hz, J_2 = 3.0 Hz, 1 H) [**IXb**: 4.45 (q, 5-CH, J_1 = 17.1 Hz, J_2 = 9.30 Hz, 1 H), 4.91 (m, 4-CH_2, 1 H), 5.15 (m, 4-CH_2, 1 H)] [26], 6.99 (tm, J = 7.2 Hz, 1 H), 7.06 (dm, J = 7.2 Hz, 2 H), 7.19 (m, 1 H), 7.24 (tm, J = 7.8 Hz, 2 H), 7.37 (dm, J = 8.1 Hz, 1 H), 7.66 (td, J_1 = 7.5 Hz, J_2 = 1.5 Hz, 1 H), 8.57 (dm, J = 5.1 Hz, 1 H); ^{13}C nmr: δ 37.1 (CH_2), 42.4 (CH), 120.3 (Ph C), 120.6 (Pyr C), 122.3 (Ph C), 122.7 (Ph C), 129.0 (Pyr C), 136.7 (Pyr C), 149.2 (Pyr C), 154.0 (Ph C), 158.8 (Pyr C).

Anal. Calcd. for $C_{13}H_{12}N_2$: C, 79.56; H, 6.16; N, 14.27. Found: C, 79.84; H, 6.21; N, 13.81.

1-(4-Chlorophenyl)-2-(4-nitrophenyl)aziridine (**Xa**).

This was obtained as an orange crystalline material, mp 112-114°; ^{1}H nmr: δ 2.41 (dd, 3-CH_2, J_1 = 3.0 Hz, J_2 = 1.2 Hz, 1 H), 2.54 (dd, 3-CH_2, J_1 = 6.6 Hz, J_2 = 1.2 Hz, 1 H), 3.16 (dd, 2-CH, J_1 = 6.6 Hz, J_2 = 3.0 Hz, 1 H) [**Xb**: 4.34 (q, 5-CH, J_1 = 16.5 Hz, J_2 = 6.90 Hz, 1 H), 4.96 (m, 4-CH_2, 2 H)] [26], 6.96 (dt, J_1 = 8.9 Hz, J_2 = 2.1 Hz, 2 H), 7.22 (dt, J_1 = 8.7 Hz, J_2 = 2.1 Hz, 2 H), 7.53 (dt, J_1 = 9.0 Hz, J_2 = 2.1 Hz, 2 H), 8.22 (dt, J_1 = 9.0 Hz, J_2 = 2.1 Hz, 2 H); ^{13}C nmr: δ 38.6 (CH_2), 41.0 (CH), 121.7 (Cl-Ph C), 123.8 (Cl-Ph C), 126.9 (O_2N-Ph C), 128.1 (Cl-Ph C), 129.2 (O_2N-Ph C), 138.0 (Cl-Ph C), 146.7 (N_2O-Ph C), 148.0 (O_2N-Ph C).

Anal. Calcd. for $C_{14}H_{11}ClN_2O_2$: C, 61.21; H, 4.04; N, 10.20. Found: C, 61.13; H, 3.99; N, 10.19.

Triazoline **Xb** was obtained as an orangish yellow solid, mp 161-163°; ^{13}C nmr: δ 57.3 (CH_2), 75.5 (CH), 116.0 (Cl-Ph C), 124.8 (Cl-Ph C), 126.9 (O_2N-Ph C), 128.1 (Cl-Ph C), 129.5 (O_2N-Ph C), 138.4 (Cl-Ph C), 146.9 (O_2N-Ph C), 147.9 (O_2N-Ph C).

Reaction of 4-Chlorophenyl Azide with 4-Vinylpyridine at Room Temperature.

Equimolar amounts (0.1 mole) of 4-chlorophenyl azide and 4-vinylpyridine were mixed in ethanol (10 ml) and allowed to stand at rt for a period of 2 months. The resulting dark brown gummy mixture was purified by column chromatography to yield

two products. The product with mp 103-105°, was identified as the aziridine **IVa** (yield 4.4%). The second product, mp 210-212°, no dec, was identified conclusively as the triazole **XI** and not a triazoline by ms and nmr (yield 5.1%).

1-(4-Chlorophenyl)-4-(4-pyridyl)triazole (**XI**).

This compound was a colorless solid, mp 210-212°; ^{1}H nmr: δ 7.55 (dd, J_1 = 6.9 Hz, J_2 = 2.1 Hz, 2 H), 7.76 (dd, J_1 = 6.9 Hz, J_2 = 2.1 Hz, 2 H), 7.80 (dd, J_1 = 4.5 Hz, J_2 = 1.8 Hz, 2 H), 8.33 (s, 5-CH, 1 H), 8.71 (dd, J_1 = 4.5 Hz, J_2 = 1.8 Hz, 2 H); ^{13}C nmr: δ 119.0, 120.0 (Ph C), 121.8 (Ph C), 130.1 (Pyr C), 135.0 (Ph C), 135.2, 137.3 (Ph C), 146.1 (Pyr C), 150.6 (Pyr C). ms (FAB): M+1 (%) 257 (M+H, 100), 229 [(M+H-28), 20].

Anal. Calcd. for $C_{13}H_9N_4Cl$: C, 60.82; H, 3.54; N, 21.83. Found: C, 60.91; H, 3.50; N, 21.81.

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