Study of the Azide Ion Reactivity Towards Heterocyclic Cations. V.
Syntheses, Thermal and Photochemical Rearrangements
of α,α'-Diphenylpyridylazidomethanes

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The syntheses of α,α'-diphenylpyridylazidomethanes are reported and the thermal and photochemical rearrangements of these azides are studied. For the thermolysis and photolysis of these azides a step by step mechanism is proposed. The differences between thermolysis and photolysis should come from the nature of the nitrenoide state involved; the $^1\Delta$ electrophilic state in thermolysis and the less selective $^1\Sigma$ diradical state in photolysis.

The thermal and photochemical rearrangements of alkylaryl azides have been studied for the last fifteen years [1-4] to elucidate the mechanism of this variant of the Stieglitz' rearrangement [5].
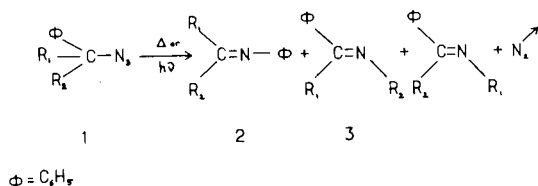

Figure 1

Literature about rearrangement mechanisms of these azides, mainly trityl azides and their derivatives, is extremely confused and, sometimes contradictory [6,7]. From previous studies, it appears that for the thermal rearrangement, a concerted mechanism with some participation of the migrating aryl group [1] would have to be rejected in favour of a step by step mechanism with a singlet nitrene intermediate [3,8].
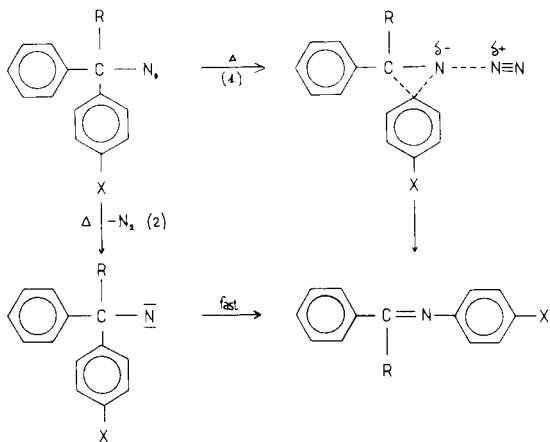

Figure 2

For the direct photochemical rearrangement of alkyl az-

ides, the electronic transition (λ = 287 nm) normally involved is π_y, π_x* [9], singlet according to Saunders and Lewis' observations [10,11]. Thus a concerted rearrangement with elimination of nitrogen will give according to Abramovitch [4] an imine in the excited state.
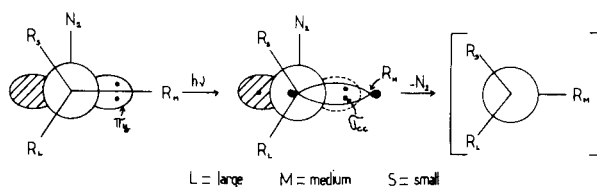

Figure 3

In this concerted migration-elimination, the migrating group and departing nitrogen molecule would be orthogonal to each other, so that the bonding orbital σ of the migrating group would overlap with the electron deficient p_y orbital (Figure 3). Assuming that the Franck Condom's principle holds in these photolyses, the migratory aptitudes would be determined by the relative populations of different conformations at the fundamental state.

To substantiate these hypotheses, we took interest in the thermal and photochemical decomposition of α,α'-diphenylpyridylazidomethanes **1** (Figure 1; R_1 = C_6H_5; **a**, R_2 = 4-pyridyl; **b**, R_2 = 3-pyridyl; **c**, R_2 = 2-pyridyl). These isomers **1** rearrange to imines **2** and **3**. The study of the rearrangement of such compounds should permit, on the one hand to evaluate the influence of electronic density around the carbons of the migrating aromatic group, and on the other hand to test the hypothesis formulated by Abramovitch [4] for the photochemical rearrangement. Steric hindrances of the pyridyl moiety and the phenyl moiety are probably the same, so that we should be expecting a statistical distribution of imines **2** and **3** during this

Table 1

Comparison of Different Irradiation Conditions of the Azide 1a

Irradiation conditions	Time minutes	Total Yield % 2 + 3	Yield % Imine 2	Yield % Imine 3
low pressure (λ = 254 nm)	30	40	73	27
medium pressure (λ > 290 nm)	90	41	68	32
medium pressure (+ 250 μl of αMe-Naph)	30	78	76	24

Table 2

Sensitized Photochemical Rearrangement of Azide 1

	Irradiation time minutes	1	3	5	10	12	20	30	45
	Conversion rate %	3	—	6	—	47	75	81	92
1a	Recovery yield % [a]	98	—	97	—	92	88	89	84
	Migration aptitude [b]	—	—	1.02	—	1.0	1.0	0.98	0.98
	Conversion rate %	—	6	9	45	—	—	100	—
1b	Recovery yield % [a]	—	96	95	97	—	—	83	—
	Migration aptitude [b]	—	1.0	1.04	1.05	—	—	0.96	—
	Conversion rate %	4	—	81	97	—	100	100	—
1c	Recovery yield % [a]	98	—	100	95	—	93	93	—
	Migration aptitude [b]	1.00	—	1.06	1.02	—	1.03	1.03	—

[a] No hydrolysis detected. [b] Correction for statistical preference.

decomposition.

Results and Discussion.

Photochemical Rearrangement of Azides 1.

The direct photolysis of azide 1a in cyclohexane solution with a low or medium pressure mercury lamp and the sensitized photolysis of this azide using α-methylnaphthalene as a singlet sensitizer and a triplet quencher, gave both imines 2a and 3a isolated and purified by thin layer chromatography (tlc) on silica with the yields recorded in Table 1. These yields are given for the total conversion rate.

a) Regardless of the type of the photolysis, the rate of imines 2 and 3 remained the same. b) The best results were obtained by using α-methylnaphthalene as a sensitizer. For the two kinds of irradiation a photodegradation was observed considering the decreasing total yield. We did not test the influence of different irradiation processes on the yields in the other two series for two reasons: on one hand imines 2b and 3b as well as imines 2c and 3c have R_f values too close to be separated by thin layer chromatography and moreover they are easily hydrolysed on silica; on the other hand the best yields in imines 2a and 3a were

obtained during the sensitized photolysis (Table 1) which led us to use this kind of photolysis in the following studies. In fact to obtain precise migration aptitudes of the pyridyl moiety (pyridyl/phenyl) low conversion (less than 10%) experiments were necessary so that we had to develop an accurate analytical method. This method must be soft to prevent the hydrolysis of imines 2b and 3b or 2c and 3c. The photo-rearrangements were followed by high performance liquid chromatography (hplc), which was achieved, regardless of the series, with silica as the stationary phase and ternary solvents as the mobile phase (isooctane as solvent, tetrahydrofuran as cosolvent and diethylamine as buffer). The results are reported in Table 2.

From Table 2 it may be observed: a) Independent of the series, the migration aptitudes of the pyridyl moiety remained the same. The photo-degradation of imines 2 and 3 was negligable, α-methylnaphthalene therefore was effective as a protector. b) Allowing for the precision of the analytical method the migration aptitudes of 4-pyridyl, 3-pyridyl and 2-pyridyl moieties were the same and equal to the unit. This statistical migration of the aryl moiety towards nitrogen may be explained in two ways: The first, in-

Table 3

Thermal Rearrangement of Azide 1 in Nitrobenzene at 200°

Azide	Total Yield %	Imine 2 %	Imine 3 %	Migration aptitude [a] of pyridyl moiety
1a	67	9	91	0.20
1b	63	30	70	0.86
1c	62	3	97	0.06

[a] Corrected for statistical preference.

Table 4

Thermolysis of Azides 1 at 200° in Dodecane

	Thermolysis time minutes	1	2	3	5	15	20	30	45	60
	Conversion rate %	—	10	—	25	—	72	86	95	—
1a	Recovery yield % [a]	—	99	—	96	—	85	82	80	—
	Migration aptitude [b]	—	0.25	—	0.21	—	0.24	0.27	0.25	—
	Conversion rate %	14	—	21	43	70	—	99	—	100
1b	Recovery yield % [a]	93	—	90	88	92	—	95	—	95
	Migration aptitude [b]	0.8	—	0.86	0.9	0.87	—	0.87	—	0.87
	Conversion rate %	7	—	—	28	72	—	89	94	100
1c	Recovery yield % [b]	100	—	—	100	92	—	88	87	82
	Migration aptitude [b]	0.13	—	—	0.15	0.13	—	0.13	0.13	0.13

[a] No hydrolysis detected. [b] Corrected for statistical preference.

volving a concerted reaction such as the Abramovitch scheme [4] i.e., in the fundamental state no conformation being favored, the phenyl and pyridyl moieties migrate in the same way. The second, involving the π electrons of the migrating moieties seems more probable, the preferential migration appearing only with an aromatic moiety [13]. As the thermal rearrangement which we will examine later, a nitrene intermediate is postulated to explain these results. The differences in selectivity between thermal and photochemical rearrangements should be due to the nature of the state of the nitrene: $^1\Sigma$ state in photolysis and $^1\Delta$ state, more selective in thermolysis.

Thermal Rearrangement of Azides 1.

The thermal decomposition rate of azides 1 was determined in two solvents with different polarities, nitrobenzene, a polar solvent and dodecane, nonpolar solvent. The rearrangement being slow below 180°, solvents with high boiling points were necessary. Regardless of the solvents used, on heating to 200°, these azides evolved nitrogen to give a mixture of imines. When the rearrangement was carried out with nitrobenzene, hplc could not be used be-

cause of solvent absorption, so that we worked until total conversion rate. Moreover the analysis of mixtures of imines 2b and 3b or 2c and 3c by tlc was not possible because they are hydrolysed on silica; these imines therefore were analysed by gas chromatography in the ketone form resulting from hydrochloric acid hydrolysis. The results are recorded in Table 3.

When the solvent used was dodecane, hplc analysis was possible since dodecane does not absorb at 254 nm, thus we could follow the thermolysis evolution from low conversion rate to total conversion rate by uv absorption at this wavelength. Table 4 shows the results.

Tables 3 and 4 show that: a) The migratory aptitudes of pyridyl moieties were independent from the duration of the thermolysis. Allowing for the analytical precision, imines 2 and 3 appeared stable during thermal decomposition. b) Taking account of the overall precision of the analysis when nitrobenzene was the solvent used, the migration aptitudes of pyridyl moieties were similar whichever type of solvent. c) The migratory ratios of 4-pyridyl (0.25), 3-pyridyl (0.85) and 2-pyridyl (0.13) moieties were

significantly different.

Up to now all the studies on the influence of the electronic density around the carbons of the migrating aromatic moieties showed that the electron donating moieties favour the migration towards nitrogen [1]. However the determining factor was not known: electronic density around the migrating carbon or overall electronic density of the migrating aromatic moiety. Moreover the influence of *meta* substituents has not been studied. The electronic distribution of pyridyl moieties may help to verify some of these hypotheses. Unlike the $\pi + \sigma$ electronic density, the π electronic density of the migrating carbons gave a linear relationship with the migratory aptitudes of the pyridyl moieties. Two mechanisms already proposed could explain these findings. a) A concerted mechanism in which the reaction would be a SN_2 reaction towards a negative center. b) A step by step mechanism in which the first step is the formation of an electrophilic nitrene and the second step, the attack by this nitrene of the electron richest center.

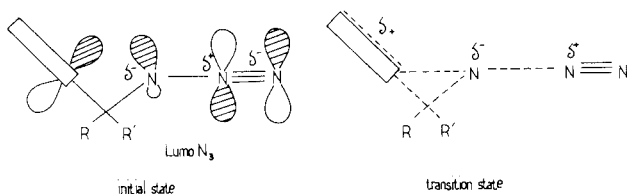initial state   transition state

Figure 4

We do not argue for the first mechanism for the following reasons: a) The differences in the migration aptitudes are small for assisted reactions [3]. b) Activation enthalpies in triarylmethylazides and methylazide decompositions are comparable, so that one might conclude there is no aryl participation in the transition state. c) A SN_2 reaction towards a negative center [14] seems most unlikely. The interaction of aromatic moieties therefore takes place when the departing nitrogen is distant. The coulombian repulsion then decreases and a bonding interaction is developed between the π electrons of the moiety and the LUMO of the generated $^1\Delta$ nitrene [14].
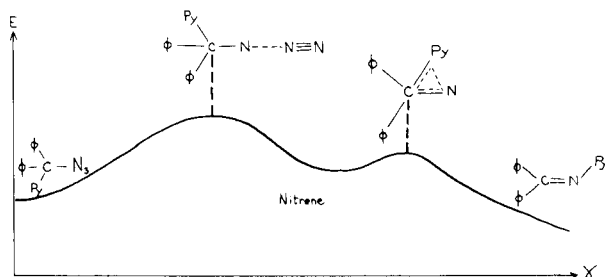

Figure 5

Conclusion.

The thermal decomposition of alkylarylazides 1 can be viewed as an electrophilic substitution on the aromatic migrating moiety by an electron deficient nitrenoid. It is worth noting that the pyridine and nitrobenzene, considered as identical substrates in regard to electrophilic substitution reactions [15] present similar migratory aptitudes (0.2 for *p*-nitrobenzene moiety and 0.25 for 4-pyridyl moiety).

As for the photochemical rearrangement, without rejecting the concerted mechanism formulated by Abramovitch [4], a step by step mechanism is proposed in thermal decomposition. The differences between thermoloysis and photolysis should come from the nature of the state of the involved nitrenoid: $^1\Delta$ electrophilic state in thermolysis and $^1\Sigma$ diradical state, less selective, in photolysis.

EXPERIMENTAL

Melting points were determined on a Kofler apparatus, calibrated with melting point standards. Infrared spectra were run on a Philips SP3 200 spectrophotometer, ultraviolet spectra on a Philips SP8 250 spectrophotometer, nmr spectra on a Bruker WP 80 spectrometer and mass spectra were recorded on AEI MS 30 or AEI MS 50 instruments. Chromatographic analyses were carried out either by a gas chromatograph equipped with a hydrogen flame ionization detector or by high performance liquid chromatograph on a Waters hplc system equipped with models 6000A pumps, WISP 710B injector and Philips PU 4020 ultraviolet detector interfaced with Hewlett Packard HP 5880 data system. During preparative lc analyses, a model R 401 refractometric detector and U6K septumless injector were used instead of ultraviolet detector and WISP injector. Lichrosol[R] Chromasolv[R] quality solvents (Merck, SDS, Fisons) were used. Microanalyses were performed by Pierre and Marie Curie University laboratories.

Synthesis of α,α'-Diphenylpyridylcarbinols 4.

α,α'-Diphenyl-4-pyridylmethanol (4a) was prepared according to the method of Villani, *et al.* [12a]. α,α'-Diphenyl-3-pyridylmethanol (3a) was prepared according to the method of MacCarty, *et al.* [12b]. α,α'-Diphenyl-2-pyridylmethanol (2a) was prepared according to the method of Tilford, *et al.* [12c].

Synthesis of Diphenyl-4-pyridylmethane Chloride.

This compound was prepared by the action of trichloromethanesulfenyl chloride with 4-pyridyldiphenylmethane according to the Traynelis method [16]. It was not possible to crystallize the oil obtained so that we modified the Traynelis procedure by purifying 4-pyridyldiphenylmethane chloride by gel permeation chromatography (gpc), under the following conditions: 2 columns (30 cm × 0.5 cm ID) of μ styragel (10 μm particule size); mobile phase, toluene; flow rate, 2 ml/min; injection of 2 ml (60 mg/ml); temperature, ambient. After two recycles, toluene was removed under vacuum and 4-pyridyldiphenylmethane chloride mp 89° was obtained in 50% yield.

α,α'-Diphenyl-4-pyridylazidomethane (1a).

A solution of 200 mg (0.75 mmole) of α,α'-diphenyl-4-pyridylmethane chloride in 2 ml of dry dimethylformamide was stirred for 24 hours with 400 mg (6.3 mmoles) of sodium azide. After extraction with ether and washing with water, the extracts were dried over magnesium sulfate. The solvent was removed to give white crystals (188 mg, 90%). Analytical and spectral properties are recorded in Table 5.

Table 5

Physical Characteristics of Azides **1**

Azides **1**		**a**	**b**	**c**
Mp °C		60	56	92
ir (potassium bromide): ν max cm^{-1} N$_3$		2100	2100	2100
uv (ether): λ max nm (log ϵ max)		260 (3.41)	260 (3.55)	360 (3.41)
nmr (deuteriochloroform): ppm		8.4-8.7 (m, 2H), 7.1-7.5 (m, 12H)	8.3-8.5 (m, 2H), 7-7.7 (m, 12H)	8.6-8.8 (m, 1H), 7-7.7 (m, 13H)
Analysis Calcd. (Found)	C	75.50 (75.28)	75.50 (75.17)	75.50 (75.35)
	H	4.93 (5.03)	4.93 (5.10)	4.93 (5.04)
	N	19.57 (19.35)	19.57 (19.47)	19.57 (19.38)
Mass spectrum m/e (%)		286 (3), 258 (6), 257 (3), 244 (100), 181 (9), 180 (14), 167 (7), 166 (11), 78 (13), 77 (27)	286 (1), 258 (11), 257 (6), 244 (100), 181 (13), 180 (9), 167 (11), 166 (27), 78 (14), 77 (33)	286 (1), 258 (38), 257 (22), 244 (100), 181 (40), 180 (25), 167 (30), 166 (58), 78 (43), 77 (70)

Table 6

Physical Characteristics of Imines **2** and **3**

Imines		**2a**	**3a**	**2b**	**3b**	**2c**	**3c**
Mp °C		118	90	124	105	100	78
ir (potassium bromide): ν max cm^{-1}		3050 1615 1595	3060 1635 1590	3060 1640 1570	3060 1630-1600 1575	3060 1640 1590	3060 1640 1590
uv (ether): λ max nm (log ϵ max)		347 (3.56) 254 (4.42)	325 (3.54) 254 (4.54)	342 (3.64) 254 (4.46)	325 (3.96) 250 (4.82)	340 (4.00) 260 (4.64)	330 (3.67) 254 (4.60)
nmr (deuteriochloroform): ppm		8.6-8.9 (m, 2H), 6.7-8 (m, 12H)	8.1-8.5 (m, 2H), 6.9-7.8 (m, 12H)	8.3-8.5 (m, 2H), 6.9-8 (m, 12H)	6.9-8.2 (m, 14H)	9 (m, 1H), 7.4-8.6 (m, 13H)	8.5 (m, 1H) 7.1-8 (m, 13H)
Analysis Calcd. (Found)	C	83.69 (83.43)	83.69 (83.99)	83.69 (83.40)	83.69 (83.42)	83.69 (83.72)	83.69 (83.83)
	H	5.46 (5.72)	5.46 (5.77)	5.46 (5.38)	5.46 (5.71)	5.46 (5.71)	5.46 (5.40)
	N	10.85 (10.56)	10.85 (10.65)	10.85 (10.61)	10.85 (10.81)	10.85 (10.59)	10.85 (10.58)
Mass spectrum m/e (%)		258 (100), 257 (11), 181 (46), 166 (9), 78 (10), 77 (2)	258 (100), 257 (36), 181 (30), 180 (86), 166 (11), 78 (13), 77 (36)	258 (78), 257 (56), 181 (40), 180 (50), 167 (9), 166 (63), 78 (16), 77 (100)	258 (100), 257 (35), 181 (98), 180 (98) 165 (65), 78 (55), 77 (12)	258 (98), 257 (70), 181 (25), 180 (100), 155 (50), 154 (15), 78 (10), 77 (80)	258 (44), 257 (100), 181 (4), 180 (17), 155 (89), 154 (55), 78 (30), 77 (5)

α,α'-Diphenylpyridylazidomethane **1b** and **1c**.

These azides were synthesized from the corresponding carbinols **4b** and **4c** by the action of sodium azide in sulfuric acid according to Galt *et al.* [17]. They were obtained in 60% and 80% yields respectively.

Preparation of Imines **2**.

These imines were synthesized from aniline and the corresponding pyridylketones according to Nageli's method [18]. However we used 4 Å molecular sieves as the drying agent. Imines **2b** and **2c** which were easily

hydrolysed on silica were purified by hplc whereas imine **2a** was purified by tlc on silica and obtained in a 60% yield.

Purification of Imine **2b**.

Imine **2b** was purified by hplc under the following conditions: two columns (30 cm × 0.4 cm ID) of Zorbax (7 μm particule size); mobile phase, isooctane/THF/diethylamine 95/4.5/0.5; flow rate, 2 ml/min; injection 2 ml (50 mg/ml); temperature, ambient; then by gpc under the following conditions: three columns (30 cm × 0.4 cm ID) of μ styragel (10 μm particule size); mobile phase, toluene; flow rate 2 ml/min; injection of 2 ml (50 mg/ml); temperature, ambient. After both purifications, the yield for imine **2b** was 50%.

Purification of Imine **2c**.

Imine **2c** was easily hydrolysed on silica, thus was purified by gpc under the same conditions as above. Colorless crystals of imine **2c** were obtained in a 70% yield.

Analytical and spectral properties of imines **2a**, **2b** and **2c** are recorded in Table 6.

Imines **3**.

These imines were synthesized from diphenyldimethoxymethane and the corresponding aminopyridines with the method described below for imine **3a**. 4-Aminopyridine (300 mg, 3.2 mmoles) and 600 mg (2.6 mmoles) of diphenyldimethoxymethane were heated in a sealed tube at 200° for four days. The reaction mixture was dissolved in dry ether and after concentration, the residual oil was chromatographed on silica (tlc) to give 217 mg of imine **3a** (32% yield). It is worth noting that imines **3b** and **3c** easily hydrolysed on silica were not purified by hplc but by gpc under the same conditions described above for imine **2c**. These imines **3b** and **3c** were obtained in 45% and 30% yields respectively.

Analytical and spectral properties of imines **3a**, **3b** and **3c** are recorded in Table 6.

Study of Azide 1 Photolysis Reaction Mixture by GC.

A solution of 50 mg (0.17 mmole) of azides **1a** to **c** and 250 μl of α-methylnaphthalene in 100 ml of dry cyclohexane was irradiated with a Philips HPLN 400 medium pressure lamp. The solvent was removed and the reaction mixture hydrolysed with 10 ml of 0.1 M hydrochloric acid. The hydrolysis was followed by tlc; elution: ethyl acetate/cyclohexane, 7/3. At the end of the hydrolysis, the solution was decanted, the aqueous layer made basic and extracted with ether. The ether solution was dried over magnesium sulfate and the ether removed. Three μl of the residual oil was dissolved in 100 μl of ether and analysed by gc under the following conditions: column SE 30 (3 m × 1/8 inch); temperature 210°; N₂ at 30 ml/min; injection of 5 μl. Analysis was achieved by using an internal standard method.

Photochemical Rearrangements of α,α'-Pyridyldiphenylazidomethane (**1a**).

Direct Photolysis.

With a Hanau TNN 15/32 Low Pressure Mercury Lamp.

A solution of 50 mg (0.17 mmole) of azide **1a** in 200 ml of dry cyclohexane was irradiated under nitrogen at room temperature for 30 minutes with a Hanau TNN 15/32 low pressure mercury lamp. The solvent was removed and the residual oil was chromatographed on silica (tlc) using ethyl acetate/cyclohexane, 7/3, as eluant. Imine **3a** (5 mg, 11%) and imine **2a** (13 mg, 29%) were obtained and compared by infrared spectrum and by melting points with authentic samples.

With a Philips HPLN 400 Medium Pressure Lamp.

A solution of 50 mg (0.17 mmole) of azide **1a** in 130 ml of dry cyclohexane was irradiated under nitrogen at ambient temperature for 90 minutes with a Philips HPLN 400 medium pressure lamp. The solvent was removed and the residual oil was chromatographed as mentioned above. Imine **3a** (6 mg, 12%) and imine **2a** (12.5 mg, 27%) were obtained.

Sensitized Photolysis.

A solution of 50 mg (0.17 mmole) of azide **1a** and 250 μl of α-methylnaphthalene in 130 ml of dry cyclohexane was irradiated under nitrogen at room temperature over a 90 minute period with a Philips HPLN 400 medium pressure lamp. The solvent was removed and the residual oil was chromatographed on silica under the same conditions as above. Imine **3a** (8 mg, 19%) and imine **2a** (24 mg, 52%) were obtained.

Kinetics Study of Sensitized Photolysis with α-Methylnaphthalene of Azides **1**.

A solution of 30 mg (0.1 mmole) of azide **1** and 250 μl of α-methylnaphthalene in 120 ml of dry cyclohexane was irradiated under a nitrogen atmosphere, at room temperature with a Philips HPLN 400 medium pressure lamp through a pyrex filter sleeve. At set time intervals, a 1 ml aliquot was taken from the reaction flask and analysed by hplc, under the following conditions: two columns (30 cm × 0.4 cm ID) of Zorbax (7 μm particle size) made according to Rocca et al. [19] (N = 9000 plates/m); mobile phase, isooctane/THF/diethylamine 90/9.5/0.5, for 4-pyridyl and 2-pyridyl series and isooctane/THF/diethylamine 99/0.5/0.5 for 3-pyridyl series; flow rate 2 ml/min for 4-pyridyl and 2-pyridyl series and 3 ml/min for 3-pyridyl series; injection, 100 μl; uv monitor at 254 nm; sensitivity 1.8 AUFS. Under these conditions resolution factor between two chromatographic peaks is ≥ 1.5.

Study of Azides **1a** to **c** Thermolysis in Nitrobenzene by GC.

In a flask connected with an apparatus which measures evolved nitrogen, a solution of 50 mg (0.17 mmole) of azides **1a**, **1b** or **1c** in 20 ml of dry nitrobenzene was heated at 200° until the nitrogen was totally evolved. The solvent was removed under vacuum and the reaction mixture hydrolysed with 10 ml of 0.1 M hydrochloric acid at 110°. The hydrolysis was followed by tlc; elution: ethyl acetate/cyclohexane, 7/3. When the hydrolysis was ended the reaction mixture was prepared and analysed in the same way as for the photolysis of azide **1**.

Thermolysis Kinetics of Azides **1**.

Fifty mg (0.17 mmole) of azides **1a**, **1b** or **1c** were introduced with stirring and under nitrogen in preheated dry dodecane at 200°. At set time intervals, a 1 ml aliquot was taken from the reaction flask and analysed under the same conditions as those for the photolysis of azides **1**.

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