Study of the Azide Ion Reactivity Towards Heterocyclic Cations. VII. Application of Thermal and Photochemical Rearrangements of α,α'-Diphenylpyridylazidomethanes to the Syntheses of 4-Pyridyldibenzoheteroazepines

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The application of thermal and photochemical rearrangements of α,α'-diphenylpyridylazidomethanes to the synthesis of 4-pyridyldibenzoheteroazepines is reported. This route provides easily the 11-(4-pyridyl)dibenzo[*b,f*][1,4]oxazepine and the 11-(4-pyridyl)dibenzo[*b,f*][1,4]thiazepine with good yields. In the case of the 11-(4-pyridyl)dibenzo[*b,f*][1,4]selenazepine this route is less interesting because of the instability of this compound. The previously proposed mechanisms for the thermal and photochemical rearrangements of α,α'-diphenylazidomethanes can be applied to the azides examined.

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Galt [1] and Coombs [2], independently in 1958, first studied the thermal rearrangements of heterocyclic azides. The studied compounds were 9-phenyl-9-azidoxanthene and 9-phenyl-9-azidothioxanthene. A few years ago, on one hand we carried out for the first time the photochemical rearrangement of heterocyclic azides, and on the other hand we extended these rearrangements to the selenoxanthylic and anthronic azides [3-7]. The purpose of these studies was to find an easy and general route to obtain heteroazepines. Among the compounds so obtained are the 11-substituted dibenzo[*f,b*][1,4]heteroazepines. Various 11-substituted dibenzo[*b,f*][1,4]heteroazepines have pharmacodynamic activities [8]. All of these dibenzo[*b,f*][1,4]heteroazepines have a cyclic or linear substituent in position 11, containing one nitrogen atom. When the substituent is cyclic, the nitrogen atom is in the δ position. Using the results of our study [9] on the photo and thermal rearrangements of the α,α'-diphenylpyridylazidomethanes, we have been interested in the synthesis of the 11-(4-pyridyl)dibenzo[*b,f*][1,4]heteroazepines. In fact, by heating or by photolysis, the 9-azido-9-(4-pyridyl)xanthene (**1a**), thioxanthene **1b**, selenoxanthene **1c** can give the desired dibenzoheteroazepines **2a** to **2c**, by ring expansion (Figure 1).

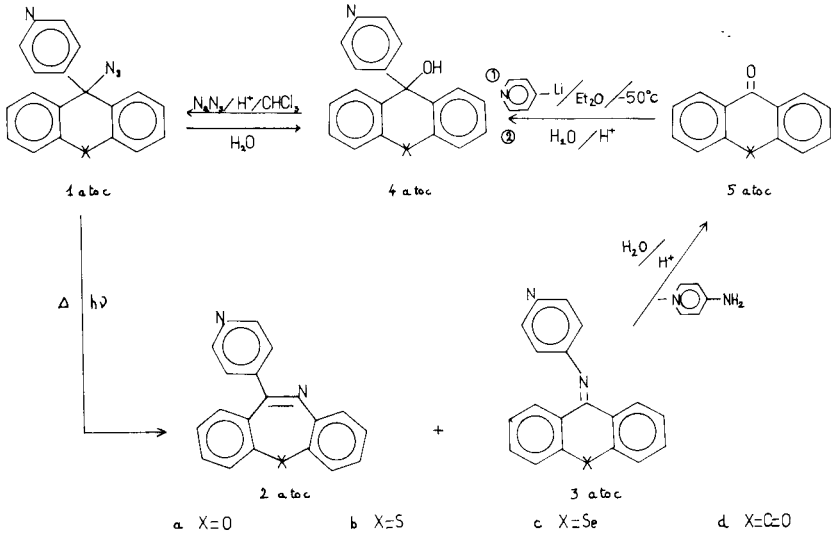

Figure 1

Synthesis of 9-(4-Pyridyl)xanthydrol (**4a**), Thioxanthydrol (**4b**), Selenoxanthydrol (**4c**) and of Their Corresponding Azides **1a** to **1c**.

The 9-(4-pyridyl)xanthydrol (**4a**), thioxanthydrol (**4b**) and selenoxanthydrol (**4c**) are all unknown. They have been synthesized according to the method of Wibaut *et al.* [10] by the action of 4-pyridyllithium at −50° with the corresponding ketones **5** (yields 30-40%).

The 4-pyridyllithium has been prepared by halogen-metal exchange at −75° between 4-bromopyridine and *n*-butyllithium in ethereal solution (Figure 2). 4-Bromopyridine, unstable above −30°, is regenerated from its chloride, stable at room temperature.

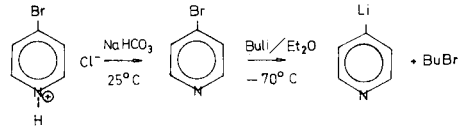

Figure 2

The corresponding azides **1a** to **1c** have been easily prepared by the action of sodium azide in sulfuric acid according to Galt *et al.* [1] with good yields. The proposed structures of these azides agree with analytical and spectral properties. Moreover these structures are confirmed by hydrolysis of these compounds in their corresponding carbinols **4a** to **4c**.

Thermal Rearrangements of 9-Azido-9-(4-pyridyl)xanthene (**1a**), Thioxanthene (**1b**) and Selenoxanthene (**1c**).

Azides **1a** to **1c** evolve nitrogen upon heating to yield dibenzo[*b*,*f*][1,4]heteroazepines **2a** to **2c** and anils **3a** to **3c**. To follow the course of the rearrangement and to obtain migration tendencies of 4-pyridyl depends (4-pyridyl/phenyl of the heterocyclic part) upon high precision and at a low conversion rate, we used high performance liquid chromatography (hplc) that we have previously developed [9].

We showed in the case of the rearrangements of 9-phenyl-9-azidoxanthene and 9-phenyl-9-azidothioxanthene [3] as well as in the case of the thermolysis of α,α′-diphenylpyridylazidomethanes [9] that the migratory aptitude was independent from the temperature of thermolysis and the nature of solvent. So we have studied only the thermal rearrangement of azides **1a** to **1c** in one apolar solvent (dodecane) and at one temperature (190°).

The results are recorded in Table 1 since in the case of the thermolysis of 9-(4-pyridyl)-9-azidoselenoxanthene (**1c**), the (4-pyridyl)dibenzo[*b*,*f*][1,4]selenazepine was not obtained absolutely pure, the analytical method similar to that developed in the case of azides **1a** and **1b** cannot be used. Thin layer chromatography on silica (tlc) was used as the analytical method at the end of the thermolysis.

Moreover during this thermolysis, (4-pyridyl)dibenzoselenazepine (**2c**) extrudes selenium to yield (4-pyridyl)phenanthridine (**6**) (Figure 3).

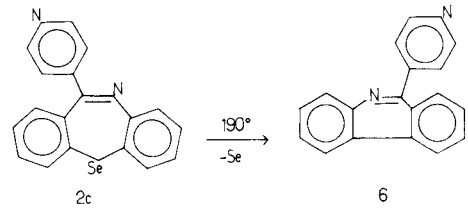

Figure 3

Such an extrusion can be followed by hplc. In fact the

Table 1

Thermal Rearrangement of Azide **1**

	Thermolysis time minutes	1	3	5	10	15	30	45	60
	Conversion rate %	23	48	67	85	95	100	100	—
1a	Recovery yield %	100	91	86	80	78	78	78	—
	Migration aptitude [a]	0.25	0.35	0.34	0.30	0.30	0.29	0.29	—
	Conversion rate %	36	69	84	—	96	—	—	100
1b	Recovery yield %	97	95	90	—	90	—	—	90
	Migration aptitude [a]	2.1	2.3	2.2	—	2.2	—	—	2.2
	Conversion rate %	—	—	—	—	—	—	—	100
1c	Recovery yield %	—	—	—	—	—	—	—	70 [b]
	Migration aptitude [a]	—	—	—	—	—	—	—	2.2 [b]

[a] Corrected for statistical preference. [b] Determined by thin layer chromatography.

comparison of the reaction mixture chromatograms after 1 minute and 8 minutes of heating shows the progressive transformation of 11-(4-pyridyl)dibenzoselenazepine (**2c**) into (4-pyridyl)phenanthridine (**6**), the anil **3c** remaining unmodified (Figure 4).

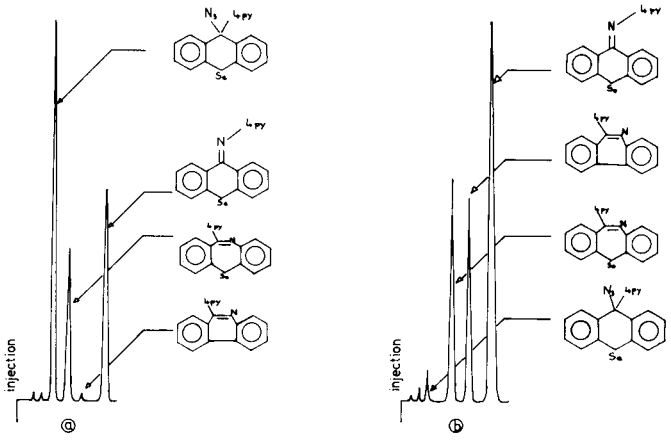

Figure 4

The structure of the unknown compounds resulting from the thermolysis of azides **1a** to **1c** agrees with their analytical and spectral properties. For the anils **3a** to **3c** the structures are confirmed by their hydrolysis into their corresponding ketones **5a** to **5c**.

Photolysis of 9-Azido-9-(4-pyridyl)xanthene (**1a**), Thioxanthene (**1b**) and Selenoxanthene (**1c**).

In recent studies [3,4 and 9] we showed that in the case of alkylazides, whether in heterocyclic series or not, the best results are obtained for sensitized photolysis; α-methylnaphthalene is effective as a singlet sensitizer, triplet quencher and protector for the reaction products.

Thus we studied the photochemical rearrangement of azides **1a** to **1c** sensitized with α-methylnaphthalene. The photolysis was carried out with a medium pressure mercury lamp. The solvent used was cyclohexane. Thus hplc analyses are possible since cyclohexane does not absorb at the detection wavelength (254 nm). The results are recorded in Table 2.

In the case of 9-azido-9-(4-pyridyl)selenoxanthene (**1c**) we have to use an analysis by tlc at total conversion rate for the same reasons as mentioned above. Photolysis of azides **1a** to **1c** leads to the same products as those of thermolysis except for (4-pyridyl)phenanthridine (**6**) which is not obtained. Aromatisation with an extrusion of selenium does not occur photochemically.

Discussion.

From the results it may be observed: 1) For thermolysis as well as photolysis of 9-azido-9-(4-pyridyl)xanthene (**1a**), thioxanthene (**1b**) and selenoxanthene (**1c**), the migration aptitute of the 4-pyridyl moiety (4-pyridyl/phenyl of the heterocyclic part) stays the same during thermolysis or photolysis, shown by the precision of the analytical method. The average values of migration aptitudes are recorded in Table 3. 2) The previously developed analytical method [9] permits the evaluation of the migration aptitude with good precision regardless of the duration of the reaction, particularly at a low conversion rate. 3) In the case of the photochemical rearrangement, the migration aptitude of the 4-pyridyl moiety stays the same and equal to 1.6 whatever the nature of the heterocycle. This value

Table 2

Sensitized Photolysis with α-Methylnaphthalene of Azides **1**

	Irradiation time minutes	1	3	5	7	8	15	20	60
	Conversion rate %	9	20	62	—	92	100	—	—
1a	Recovery yield %	100	101	87	—	80	74	—	—
	Migration aptitude [a]	— [b]	1.71	1.71	—	1.72	1.68	—	—
	Conversion rate %	—	2	3	6	—	45	64	80
1b	Recovery yield %	—	100	101	100	—	93	100	90
	Migration aptitude [a]	—	1.5	1.6	1.6	—	1.6	1.6	1.6
	Conversion rate %	—	—	—	—	—	—	—	100
1c	Recovery yield %	—	—	—	—	—	—	—	57 [c]
	Migration aptitude [a]	—	—	—	—	—	—	—	1.6 [c]

[a] Corrected for statistical preference. [c] The chromatographic peak surfaces can not be measured with an accurate precision. [c] Determined by thin layer chromatography.

Table 3

Average Migration Aptitude
(4-Pyridyl/phenyl of Heterocyclic Part)

X	O	S	Se
Rearrangement			
hν	1.7	1.6	1.6
Δ	0.30	2.2	2.2

close to unity and invariant with the electronic distribution argues in favour of a concerted mechanism proposed by Abramovitch [11]. It can be explained by a prefered ground state conformation of these azides at the fundamental state. This hypothesis cannot be verified now because we do not know the stereochemistry of these azides.

However, such a value of the migration aptitude is not in total contradiction with the mechanism that we have proposed in the case of tertiary alkyl azides [9]. This mechanism involves a nitrene or nitrenoid in a $^1\Sigma$ [12] diradical state, so less selective. 4) For thermolysis, the migration aptitude of the 4-pyridyl moiety varies with the heteroatom. The values recorded in Table 3 must be compared with those found in the case of 9-azido-9-phenylxanthene, thioxanthene and selenoxanthene [4] (Table 4).

Table 4

Migration Aptitude (Phenyl Substituent/Phenyl of Heterocyclic Part) Obtained in the Case of the Thermal Rearrangement of 9-Azido 9-Phenylxanthene and Homologues

X	O	S	Se
Migration aptitudes [a]	0.74	12.5	16.7

[a] Determined at total conversion rate by tlc.

Whatever the substituent in position 9, the migration aptitude increases from oxygen to selenium. However in the case of 9-azido-9-(4-pyridyl)selenoxanthene, because of the moderate total yield, the migration aptitude of the 4-pyridyl moiety is certainly mistaken but nevertheless this value is close to the value found in the 9-azido-9-(4-pyridyl)thioxanthene thermolysis. So, whatever the heteroatom, it appears that the 4-pyridyl substituent migrates less easily than the phenyl substituent. These observed results confirm that the migration aptitude depends from the π electron density of the substituent as in the case of tertiary pyridyl alkyl azides [9]. So the step by step mechanism involving a nitrene or nitrenoid in a $^1\Delta$ electrophilic state, that we have previously postulated [9], accounts for these results.

Conclusion.

From a synthetic point of view, the thermal as well as photochemical rearrangements of xanthylic, thioxanthylic or selenoxanthylic azides with a 4-pyridyl substituent are an easy route to obtain the corresponding 11-(4-pyridyl)dibenzo[*b*,*f*][1,4]heteroazepines, some of them can show pharmacological activities. The way chosen in order to obtain the best yield will depend on the nature of the desired heterocyclic framework.

From a mechanistic point of view, the present work permits us to confirm the hypotheses that we have previously proposed [9], so resumed. Thermolysis or photolysis leads to a nitrene or a nitrenoid. The easiest evolution route of these compounds involves the formation of imines. The observed differences between thermolysis and photolysis should come from the nature of the state of the involved nitrenoid: ($^1\Delta$ or $^1\Sigma$). However for the photolysis, the results cannot permit us to rule out the concerted mechanism proposed by Abramovitch [11].

EXPERIMENTAL

Melting points were determined on a Kofler apparatus, calibrated with melting points standards. Infrared spectra were run on a Philips SP3 200 spectrophotometer, ultraviolet-visible 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. Microanalyses were performed by Pierre and Marie Curie University laboratories. High performance liquid chromatography analyses were carried out on a Waters hplc system equipped with model 6000A pump, Wisp 710 B injector and Philips PU 4020 ultraviolet detector interfaced with Hewlett Packard HP 5880 data system. Lichrosol^R Chromasolv^R quality solvents (Merck, SDS, Fisons) were used without purification.

Synthesis of 4-Pyridyllithium.

4-Pyridyllithium was prepared by halogen-metal exchange between 4-bromopyridine and *n*-butyllithium according to the Wibaut *et al.* method [10].

a) Preparation of an Ethereal Solution of 4-Bromopyridine.

4-Bromopyridine hydrochloride (6.3 g, 32 mmoles) was dissolved in 100 ml of a 10% sodium bicarbonate solution. The liberated 4-bromopyridine was taken up with a syringe after two decantations and dissolved in 40 ml of dry ether. The ethereal solution was dried under stirring and free from light for 24 hours over a mixture of Drierite and magnesium sulfate.

b) Synthesis of *n*-Butyllithium.

n-Butyllithium was prepared at −10° and titrated according to the method of Gilman *et al.* [13].

c) Halogen-metal Exchange at Low Temperature.

A solution of 3.5 g of 4-bromopyridyne (20 mmoles) in dry ether prepared as above described was filtered under a nitrogen atmosphere and cooled at −75°. Thirty ml of 0.7 *M* *n*-butyllithium (20 mmoles) cooled at −75° was added under a nitrogen atmosphere and stirring for a period of 30 minutes. The colour of the reaction mixture became yellow. The reaction mixture was held at −75° for 2 hours.

Synthesis of 9-(4-Pyridyl)xanthydrol (**4a**), Thioxanthydrol (**4b**) and Selenoxanthydrol (**4c**).

These carbinols were synthesized from the corresponding ketones by the action of 4-pyridyllithium whose synthesis is described above. The selenoxanthone (**5c**) was prepared as described by Lesser [14]. Ketones **5** (3.2 g, 20 mmoles) were added during 30 minutes with stirring and under a nitrogen atmosphere to the ethereal solution of 4-pyridyllithium. The

Table 5

Physical Characteristics of Carbinols **4**

Carbinols **4**		**a**	**b**	**c**
Mp °C		263	270	271
ir (potassium bromide): ν max cm^{-1}		3060 2810 1600	3060 2810 1600	3060-3140 2750 1580
uv (ether): λ max nm (log ϵ max)		290 (3.441) 281 (3.317) 226 (4.061)	293 (3.399) 265 (4.035)	270 (3.753) 255 (3.814)
nmr (deuteriochloroform): ppm		8.4-8.7 (m, 2H), 7.15-7.5 (m, 10H), 7.1 (s, 1H) [a]	8.4-8.6 (m, 2H), 6.8-8.3 (m, 10H), 7.2 (s, 1H) [a]	8.3-8.4 (m, 2H), 6.7-8.2 (m, 10H), 7.1 (s, 1H) [a]
		$C_{18}H_{13}NO_2$	$C_{18}H_{13}NSO$	$C_{18}H_{13}NSeO$
Analysis	C	78.53 (78.44)	74.22 (74.44)	63.90 (64.04)
Calcd. (Found)	H	4.76 (4.90)	4.46 (4.46)	3.85 (3.80)
	N	5.09 (5.20)	4.81 (4.72)	4.14 (4.24)
Mass spectrum m/e (%)		275 (3), 258 (100), 197 (33), 181 (66), 105 (16)	291 (12), 275 (60), 213 (100)	339 (30), 322 (100), 261 (90)

[a] Can exchange with deuterium oxide.

Table 6

Physical Characteristics of Azide **1**

Azide **1**		**a**	**b**	**c**
Mp °C		104	120	114
ir (potassium bromide): ν max cm^{-1}		2100	2100	2100
uv (ether): λ max nm (log ϵ max)		295 (3.36) 254 (4.1)	295 (3.86) 265 (4.33)	295 (3.70) 260 (4.20)
nmr (deuteriochloroform): ppm		8.4-8.6 (m, 2H), 7-8 (m, 10H)	8.5-8.7 (m, 2H), 6.9-8 (m, 10H)	8.3-8.5 (m, 2H), 6.8-7.8 (m, 10H)
		$C_{18}H_{12}N_4O$	$C_{18}H_{12}N_4S$	$C_{18}H_{12}N_4Se$
Analysis	C	71.99 (71.72)	68.34 (68.51)	59.55 (59.25)
Calcd. (Found)	H	4.03 (4.30)	3.82 (3.75)	3.33 (3.53)
	N	18.66 (18.77)	17.71 (17.53)	15.43 (15.55)
Mass spectrum m/e (%)		300 (4), 272 (4), 258 (100), 180 (53)	316 (12), 388 (4), 374 (100), 197 (50)	364 (1), 336 (5), 322 (100), 255 (18), 245 (18), 241 (20)

colour of the reaction mixture became ochre, red or brown according to the nature of the ketones added **5a, 5b** or **5c**. The mixture was stirred for 30 minutes at −75° then for two hours at −40°. The reaction mixture was allowed to warm up to 0° and 10% hydrochloric acid was added. After decantation the ethereal layer was washed several times with a solution of sulfuric aicd. The combined aqueous layers were filtered to remove unchanged ketone and they were made basic. Carbinols **4a** and **4c** were obtained in 45% yields and carbinol **4b** within a yield of 50%. Analytical and spectral properties are recorded in Table 5.

Synthesis of 9-Azido-9-(4-pyridyl)xanthene (**1a**), Thioxanthene (**1b**) and Selenoxanthene (**1c**).

These azides were synthesized from the corresponding carbinols **4a** to **4c** by the action of sodium azide in sulfuric acid according to the method of Galt *et al.* [1]. They were obtained in 70% to 80% yields. Analytical and spectral properties of azides **1a** to **1c** are recorded in Table 6.

Thermal Rearrangement of Azide **1a** at Total Conversion Rate. Synthesis of Dibenz[*b*,*f*][1,4]oxazepine **2a** and Anil **3a**.

In a flask connected with an apparatus which measures evolved nitrogen, a solution of 100 mg of azide **1a** (10.33 mmoles) in 20 ml of dry nitrobenzene was heated at 200° until the nitrogen was totally evolved. The solvent was removed under vacuum and the residual oil was chromatographed on silica (tlc) using ethyl acetate/cyclohexane, 7/3, as the mobile phase. Dibenzo[*b*,*f*][1,4]oxazepine **2a** and anil **3a** were obtained within 70% and 10% yields respectively.

The analytical and spectral properties of dibenzo[b,f][1,4]heteroazepine **2a** and anil **3a** are recorded in Tables 7 and 8.

Table 7

Physical Characteristics of Dibenzo[b,f]heteroazepine **2**

Heteroazepine **2**		**a**	**b**
Mp °C		114	164
ir (potassium bromide): ν max cm^{-1}		3050 1600 1550	3050 1620-1600 1560
uv (ether): λ max nm (log ϵ max)		350 (2.79) 260 (3.30) 240 (3.40)	360 (3.9) 245 (4.65)
nmr (deuteriochloroform): ppm		8.6-8.9 (m, 2H), 7-7.9 (m, 10H)	8.8-9 (m, 2H), 7.2-8 (m, 10H)
		$C_{18}H_{12}N_2O$	$C_{18}H_{12}N_2S$
Analysis	C	79.39 (79.56)	75.00 (75.40)
Calcd. (Found)	H	4.44 (4.61)	4.16 (4.06)
	N	10.29 (10.47)	9.72 (9.52)
Mass spectrum m/e (%)		272 (100), 271 (78), 255 (5)	288 (100), 287 (60), 256 (21), 255 (8)

Table 8

Physical Characteristics of Anil **3**

Anil **3**		**a**	**b**
Mp °C		198	130
ir (potassium bromide): ν max cm^{-1}		3060 1620-1640 1590-1600	3060 1620 1590
uv (ether): λ max nm (log ϵ max)		340 (3.80) 240 (4.50)	360 (3.76) 265 (4.46) 245 (4.55)
nmr (deuteriochloroform): ppm		8.4-8.6 (m, 2H) 6.2-7.9 (m, 10H)	8.4-8.5 (m, 2H) 6.7-7.8 (m, 10H)
High resolution mass spectra $M^{+\cdot}$ Calcd. (Found)		272.0950 (272.09466)	288.0721 (288.07184)
Mass spectrum m/e (%)		272 (82), 271 (100), 255 (10)	288 (70), 287 (100)
		$C_{18}H_{12}N_2O$	$C_{18}H_{12}N_2S$
Analysis	C	79.41 (79.53)	75.00 (75.29)
Calcd. (Found)	H	4.41 (4.64)	4.17 (4.12)
	N	10.29 (10.51)	9.72 (10.01)

Thermal Rearrangement of Azide **1b** at Total Conversion Rate. Synthesis of Dibenzo[b,f][1,4]thiazepine **2b** and Anil **3b**.

Dibenzo[b,f][1,4]thiazepine **2b** and anil **3b** were obtained from the thermolysis of 100 mg of azide **1b** (0.32 mmoles) under the same conditions as above and chromatographed on silica (tlc) using ethyl acetate/cyclohexane, 1/1, as the mobile phase, with 41% and 35% yields respectively.

The analytical and spectral properties of dibenzo[b,f][1,4]thiazepine **2b** and anil **3b** are recorded in Tables 7 and 8.

Study of the Evolution in the Time of Sensitized Photolysis with α-Methylnaphthalene of Azides **1a** and **1b**.

A solution of 100 mg of azide (0.11 mmole) 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 mercury 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 length × 0.4 cm ID) of Zorbax (7 μm particule size) filled according to Rocca *et al.* [15], (N = 27000 plates/m); mobile phase: isooctane/THF/diethylamine 85/14.5/-0.5; flow rate: 2 ml/minute, injection: 100 μl; uv monitor at 254 nm. Under these conditions resolution factor between the two chromatographic peaks is ≥ 3.8.

Study of the Evolution in the Time of Thermolysis of Azides **1a** and **1b**.

Fifty mg of azide **1a** or **1b** (0.165 mmole) was introduced with stirring and under a nitrogen atmosphere in 200 ml of preheated dry dodecane at 200°. At set time intervals, a 1 ml aliquot was taken from the reaction flask and analysed as above.

Thermal Rearrangement of Azide **1c** at Total Conversion Rate.

In a flask connected with an apparatus which measures evolved nitrogen, a solution of 100 mg of azide **1c** (0.27 mmole) in 200 ml of dry dodecane was heated at 200° until the nitrogen was totally evolved. The solvent was removed under vacuum and the residual oil was chromatographed on silica (tlc) using ethyl acetate as the mobile phase. 9-(4-Pyridyl)-phenanthridine **6** and anil **3c** were obtained in 33% and 37% yields respectively.

The analytical and spectral properties of anil **3c** are, mp 200°; ir (potassium bromide): 3060, 1620 and 1580 cm^{-1}; uv (ether): λ max (log ϵ max) 360 (3.88), 260 (4.32); nmr (deuteriochloroform/HMDS): 8.4-8.7 ppm (m, 2H), 6.7-7.7 ppm (m, 10H); ms: (70 eV) m/e (%) 336 (18), 337 (21), 256 (100), 255 (92); high resolution mass spectra $M^{+\cdot}$: Calcd.: 336.0165. Found: 336.0167.

Anal. Calcd. for $C_{18}H_{12}N_2Se$: C, 64.48; H, 3.58; N, 8.36. Found: C, 64.27; H, 3.29; N, 8.09.

The analytical and spectral properties of phenanthridine **6** are, mp 164°; ir: (potassium bromide): 3060, 1600 and 1590 cm^{-1}; uv (ether): λ max (log ϵ max) 350 (3.22), 333 (3.32), 294 (3.77); nmr (deuteriochloroform/HMDS): 8.6-8.9 ppm (m, 4H), 8.2-8.3 ppm (m, 1H), 7.6-8.1 ppm (m, 7H); ms: (70 eV) m/e (%) 256 (100), 178 (10); high resolution mass spectra $M^{+\cdot}$: Calcd. 256.1000. Found: 256.0996.

Anal. Calcd. for $C_{18}H_{12}N_2$: C, 84.38; H, 4.69; N, 10.94. Found: C, 84.60; H, 4.58; N, 10.68.

Hydrolysis of Anils **3**.

Ten mg of anils **3** were hydrolysed by 0.1 *M* sulfuric acid at 100°. The solution made basic was extracted with ether. The corresponding ketones **5** were obtained in 95% yields and compared with authentic samples.

Extrusion of Selenium from 11-(4-Pyridyl)dibenzo[b,f][1,4]selenazepine (**2c**).

A solution of 10 mg of 11-(4-pyridyl)dibenzo[b,f][1,4]selenazepine (**2c**) in 1 ml of dry dodecane was heated at 200°. The reaction was followed by hplc analysis and the products were identified by their retention times. The analysis conditions were the same as those for thermolysis studies of azides **1a** and **1b**.

Sensitized Photochemical Rearrangement of Azide **1c** at Total Conversion Rate.

A solution containing 159 mg of azide **1c** (0.44 mmole) and 250 μl of α-methylnaphthalene in 120 ml of dry cyclohexane was irradiated under a nitrogen atmosphere at room temperature for 120 minutes with a Philips HPLN 400 medium pressure mercury lamp. The solvent was removed and the residual oil was chromatographed on silica (tlc) using cyclohexane/ethyl acetate, 7/3, as the mobile phase. Two more crystalline compounds were obtained. They crystallize after another chromatography on silica (tlc) using cyclohexane/ethyl acetate 1/1 as eluant. 11-(4-Pyridyl)dibenzo[*b*,*f*][1,4]selenazepine (**2c**) and anil **3c** were obtained in 32% and 25% yields respectively.

Some analytical and spectral properties of 11-(4-pyridyl)dibenzo-[*b*,*f*][1,4]selenazepine (**2c**), which does not satisfy the elemental analysis requirements are given below; high resolution mass spectra $M^{+\cdot}$: Calcd: 336.0165 and 334.0173. Found: 336.0168 and 334.01708; ir (potassium bromide): 3040, 1590 and 1540 cm^{-1}; nmr (deuteriochloroform/HDMS): 8.8 ppm (m, 2H), 7.2-8 ppm (m, 10H); ms: (70 eV) m/e (%) 336 (26), 335 (16), 256 (83), 255 (100).

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