

Geometrical Isomerism and Photochemical Behaviour of α -Substituted 2 and 4-Styrylpyridines.

G. Galiazzo, P. Bortolus, G. Cauzzo and U. Mazzucato

Institute of Organic Chemistry, University of Padova, Institute of Physical Chemistry, University of Padova
Laboratory of Photochemistry and High Energy Radiations of the "Consiglio Nazionale delle Ricerche", Bologna

α -Methyl and α -phenyl substituted 2 and 4-styrylpyridines were prepared by classical routes. The geometrical isomers were separated and characterized on the basis of their U.V. absorption spectra and/or of their behaviour under U.V. irradiation which led to photoisomerization and photocyclization products. The last photoreaction, in the case of α -phenyl derivatives, gave pyridyl-substituted phenanthrenes and phenyl-substituted azaphenanthrenes which were isolated and characterized.

Spectral, chromatographic and physical properties of *trans* and *cis* derivatives and related photocyclization products are given as well as some kinetic data for the photochemical reactions.

Introduction.

In recent years, we have been interested in the kinetics and mechanism of *cis-trans* photoisomerization and phenanthrenic photocyclization of stilbene-like molecules. In a previous paper the quantum yields of the two competitive photoreactions for the three isomeric styrylpyridines (stilbazoles) and some of their derivatives were reported (1,2). We now report on the geometrical isomerism and cyclization of styrylpyridines methyl- and phenyl-substituted at the ethylenic carbon in the α -position with respect to the pyridine ring. The particular aim of this work was to assign the geometrical configuration of these tri-substituted ethylenes and to isolate and characterize, in the case of α -phenyl derivatives, the different cyclized photoisomers, establishing also their relative yield, which gives useful information on the relative photocyclization kinetics.

Although a mixture of both geometrical isomers is probably obtained in the chemical synthesis (see also Ref. 3), no *cis-trans* characterization was found in the literature for α -substituted 2 and 4-styrylpyridines. Only in the case of 3-styrylpyridines has the geometrical structure (*cis* or *trans* position of the pyridine and benzene rings with respect to the double bond) been assigned on the basis of their U.V. spectra and confirmed by chemical transformation (4). The simple I.R. analysis (5) based on the C-H bending absorption at 965 cm^{-1} is not applicable here owing to the α -substitution.

The assignment of the *cis-trans* configuration of our

compounds was based on U.V. spectrophotometry and supported by their kinetic behaviour under U.V. irradiation. The structure of the photocyclization products, separated by thin layer and column chromatography, was checked in some cases by N.M.R. analysis.

Results.

A. α -Methyl Derivatives.

These compounds were prepared initially by Phillips (6) using the Shaw condensation (7), but no data on their geometrical structure were reported.

The Phillips syntheses have now been repeated in very good yield (>90%). Thin layer chromatography revealed at this stage, in the case of both 2 and 4-styrylpyridines, the presence of two products (probably, the geometrical isomers) in different amounts. The two spots were irradiated by 254 nm light and the formation of the cyclized derivatives was followed through their fluorescence; the compound present in lesser amounts was probably the *cis*-isomer. Actually, when equal amounts of the two products were spotted on the plate and then irradiated at 254 nm, the *cis*-isomer appeared to photocyclize at a faster rate. It is well known that photocyclization of stilbene-like molecules proceeds through the *cis* form while the *trans* isomer isomerizes to *cis* before cyclizing. This behaviour can be utilized in the geometrical assignment (see below).

The reaction mixture obtained in the preparation was

TABLE 1

Quantum yields of Photoisomerization and Photocyclization for α -Methyl and α -Phenyl-substituted 2- and 4-Styrylpyridines in *n*-Hexane at 254 nm.

Compounds	$\Phi_{t \rightarrow c}$	$\Phi_{c \rightarrow t}$	$\Phi_{cycl.}$
2-styrylpyridine (2)	0.23	0.24	0.01 ₄
4-styrylpyridine (2)	0.39	0.34	0.01 ₅
α -methyl-2-styrylpyridine (2)	0.22	0.14	0.09 ₅
α -methyl-4-styrylpyridine (2)	>0.5	0.09	0.15
<i>trans</i> - α -phenyl-2-styrylpyridine	0.02	—	0.01 ₃
<i>cis</i> - α -phenyl-2-styrylpyridine	—	0.16	0.02 ₃
<i>trans</i> - α -phenyl-4-styrylpyridine	—	—	0.05 ₃
<i>cis</i> - α -phenyl-4-styrylpyridine	—	—	0.06 ₆

TABLE 2

cis and *trans* α -Methyl-2- and 4-Styrylpyridines

No.	Compound	Elemental analysis						Yield %	M.P.	hRf(a)
		Calculated			Found					
		C	H	N	C	H	N			
1	<i>trans</i> - α -Methyl-2-styrylpyridine	86.10	6.70	7.17	86.50	6.75	7.08	84.9	42-43 (b)	61
2	<i>cis</i> - α -Methyl-2-styrylpyridine	86.10	6.70	7.17	86.00	6.80	7.10	6.3	57-58	71
3	<i>trans</i> - α -Methyl-4-styrylpyridine	86.10	6.70	7.17	85.90	6.60	7.14	91	73-74 (c)	58
4	<i>cis</i> - α -Methyl-4-styrylpyridine	86.10	6.70	7.17	86.30	6.80	7.10	2.2	39-40	65

(a) The hRf refer to the eluent: butanol-water-acetic acid (80:20:20). (b) The compound was liquid according to Phillips (6). (c) The melting point was 72-73° according to Phillips (6).

TABLE 3

cis and *trans* α -Phenyl-2- and 4-Styrylpyridines.

No.	Compound	Total yield %	Elemental analysis						M.P.	hRf(a)
			Calculated			Found				
			C	H	N	C	H	N		
1	<i>trans</i> - α -phenyl-2-styrylpyridine	88	88.68	5.85	5.45	88.30	5.85	5.51	liquid	55
2	<i>cis</i> - α -phenyl-2-styrylpyridine		88.68	5.85	5.45	88.50	5.70	5.28	94-95	61
3	<i>trans</i> - α -phenyl-4-styrylpyridine	86	88.68	5.85	5.45	88.70	5.67	5.43	84-86	75
4	<i>cis</i> - α -phenyl-4-styrylpyridine		88.68	5.85	5.45	88.40	5.83	5.40	98-100	63

(a) The hRf refers to the eluent: butanol-water-acetic acid (80:20:20).

TABLE 4

Phenylazaphenanthrenes and Pyridylphenanthrenes
Derived from α -Phenyl-2- and 4-Styrylpyridines

Compound	Elemental Analysis						M.P.	hRf (a)
	Calculated			Found				
	C	H	N	C	H	N		
10-Phenyl-1-azaphenanthrene	89.40	5.10	5.50	89.32	5.07	5.40	113-114	48
10-(2-pyridyl)phenanthrene	89.40	5.10	5.50	89.81	5.04	5.40	87-89	52
10-Phenyl-3-azaphenanthrene	89.40	5.10	5.50	89.30	5.20	5.45	92-94	70
10-(4-pyridyl)phenanthrene	89.40	5.10	5.50	88.90	5.20	5.30	156-157	67

(a) The hRf refer to the eluent: butanol-water-acetic acid (80:20:20).

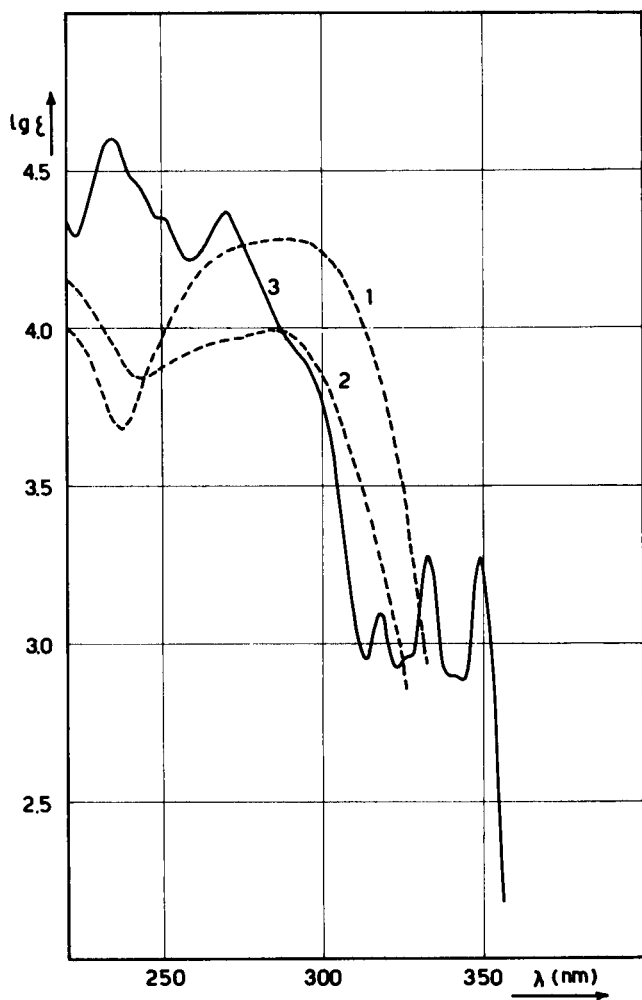


Figure 1. Absorption spectra of *trans* (curve 1) and *cis* (curve 2)- α -methyl-2-styrylpyridine and of the photocyclization product, 10-methyl-1-azaphenanthrene (curve 3) in *n*-hexane.

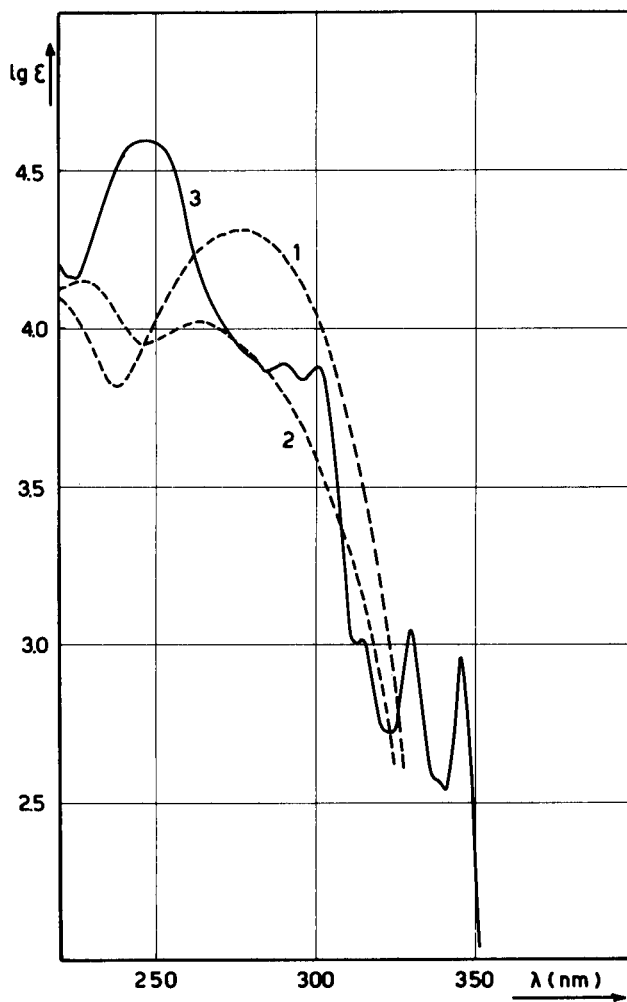


Figure 2. Absorption spectra of *trans* (curve 1) and *cis* (curve 2)- α -methyl-4-styrylpyridine and of the photocyclization product, 10-methyl-3-azaphenanthrene (curve 3) in *n*-hexane.

enriched photochemically with the *cis*-isomer and the two isomers were successively separated and identified.

Figures 1 and 2 show the spectra of *cis* and *trans* α -methyl-2- and 4-styrylpyridine; the hypsochromic shift confirms, also by comparison with the spectra of the unsubstituted derivatives (5,8), the *cis* assignment for the compound present in a smaller amount in the reaction mixture.

Table 2 reports other physical properties of the two isomers. Comparison of the melting points with those reported by Phillips (6), indicates that his reaction product was a mixture of the two isomers much enriched in the *trans* form, just as found in the present case.

The *cis* and *trans* derivatives were irradiated separately in *n*-hexane and the course of their photochemical reactions spectroscopically and chromatographically followed.

Figure 3 shows the kinetic behaviour under 254 nm irradiation of α -methyl-4-styrylpyridine (9): the spectra, registered at various irradiation times, indicate that the *cis* isomer is directly transformed into the cyclized compound, while, on the contrary, on irradiation of the *trans* isomer, an isobestic point is observed between the isomeric pair in the first reaction stages and only subsequently is the second isobestic point with the cyclized product observed. The final compounds, 10-methyl-1-azaphenanthrene and 10-methyl-3-azaphenanthrene, (see spectra in Figures 1 and 2) have been identified by comparison with literature data (10). Photodimerization was not observed even under the conditions described by Williams for unsubstituted compounds. (11)

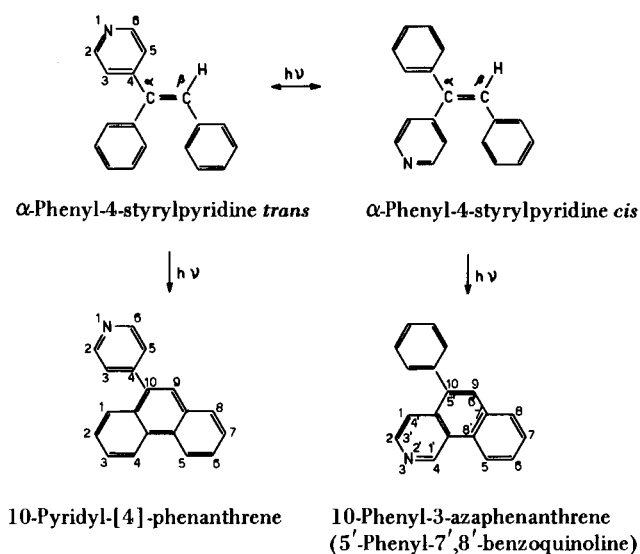
In conclusion, the kinetic behaviour and in particular the U.V. analysis support the unambiguous *cis-trans* assignment of configuration reported in figures 1 and 2 and in Table 2.

Table 1 shows the quantum yields for the competitive photochemical reactions, *cis-trans* isomerization and dehydrocyclization (2). The values for unsubstituted styrylpyridines (2) are also reported for comparison purposes. It is interesting to note that the α -methyl substitution appreciably decreases the rate of geometrical conversion whereas it enhances the rate of cyclization; this offers a convenient way for the preparation of azaphenanthrenes (12, 13).

B. α -Phenyl Derivatives.

These compounds were initially synthesized by Koenigs *et al.* (14), but no *cis-trans* characterization had been performed. We used the Shaw method which led to higher yields. Once again, two spots appeared in the thin layer analysis, though less resolved than in the case of the α -methyl derivatives, which were probably due to the *cis* and *trans*-isomers. In this case both isomers can photocyclize directly giving a pyridyl-substituted phenanthrene (from *trans* compounds, which could also be considered

as *cis* α -pyridyl stilbenes) or a phenyl-substituted azaphenanthrene (from *cis* compounds), respectively, as shown for 4-styrylpyridine derivatives:



Actually, irradiation of both spots by 254 nm light led to fluorescent photoproducts, though at different rates (see below).

The separation of the pair of isomeric styrylpyridines was successfully accomplished by column chromatography.

Table 3 reports the physical properties and Figures 4 and 5 the absorption spectra of the four separated compounds. As the spectral differences between the *cis* and *trans* isomers are very small, no unequivocal assignment of geometrical configuration can be made. Only in the case of α -phenyl-2-styrylpyridine, comparison with the spectra of the unsubstituted compounds reasonably indicates a *trans* structure for the liquid isomer prevalent in the reaction mixture.

If the spectral analysis is carried out in acid medium, in which the protonation of styrylpyridines leads to noticeable modifications of the absorption spectra (5), a complete assignment is reasonably possible. The spectra in acid medium of *cis*- α -methyl styrylpyridines, for whose characterization no serious doubt exists, show a lower intensity of the long wavelength absorption bands, with respect to the *trans* isomers, due to the protonation. Since the spectra of α -phenyl-styrylpyridines reveal similar features in acid medium (see Figure 6 as an example for both α -methyl and α -phenyl-2-styrylpyridine) the conclusions can be drawn which are reported in Figures 4 and 5 and Table 3, assigning the *trans* structure to the major product, both for α -phenyl-2- and 4-styrylpyridine.

Under U.V. irradiation of the pure compounds, photoisomerization and photocyclization occur simultaneously. Prolonged irradiation of both isomers on a preparative

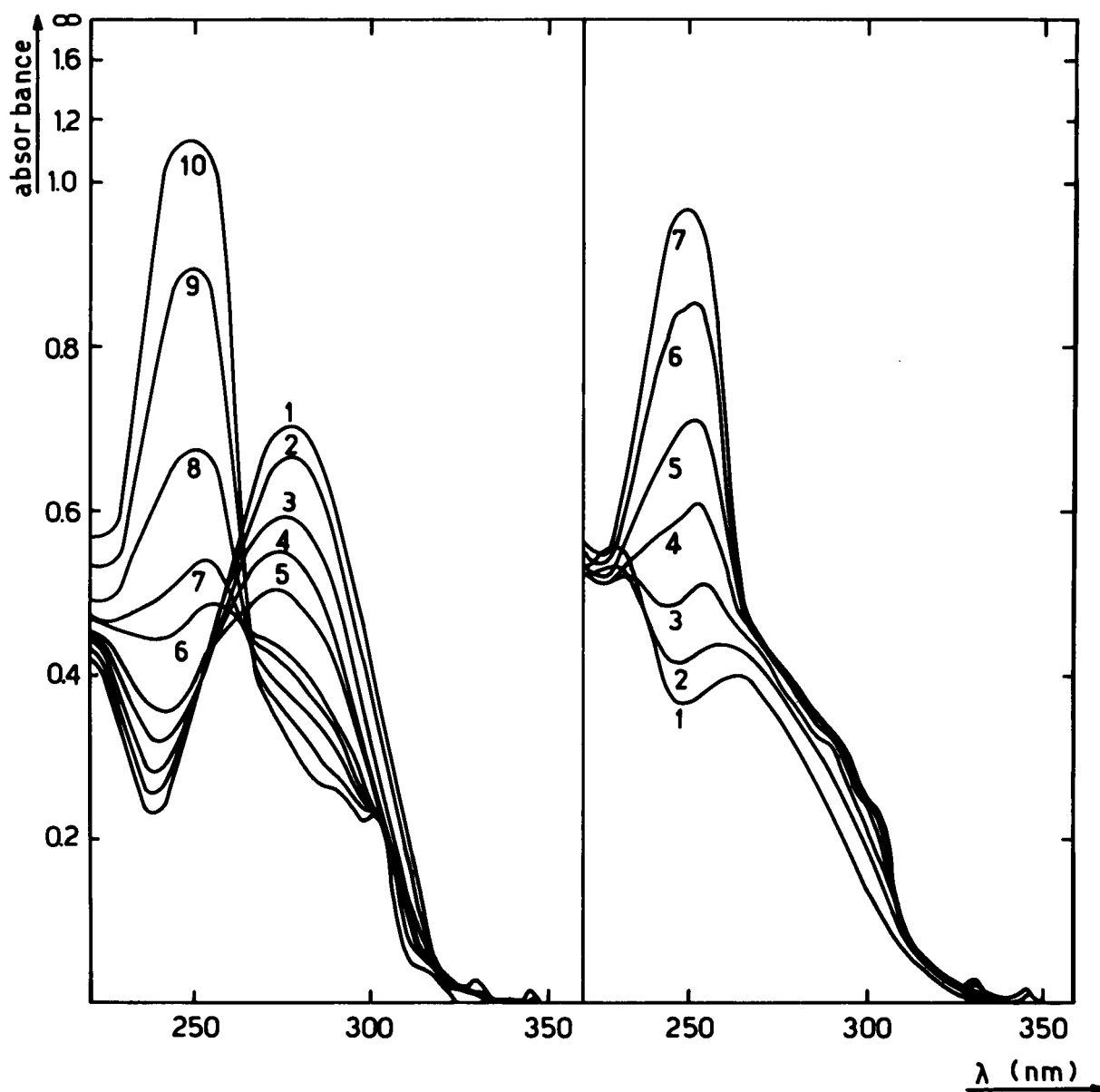


Figure 3. Typical run showing photochemical behaviour under 254 nm irradiation. Absorption spectra were recorded at successive irradiation times, starting from *trans* (a) and *cis* (b)- α -methyl-4-styrylpyridine in *n*-hexane.

scale followed by column chromatography led to the separation of two cyclized products whose structure was substantiated by elemental and spectral (N.M.R. (15) and/or U.V.) analysis.

Starting from α -phenyl-2-styrylpyridine, the photocyclization led to the 10-phenyl-1-azaphenanthrene and 10-(2-pyridyl)phenanthrene (from the *cis* and *trans* isomers, respectively) whereas from the α -phenyl-4-styrylpyridine, the 10-phenyl-3-azaphenanthrene and 10-(4-pyridyl)phenanthrene were obtained. The photocyclization products, which predominate in both preparations, appeared, on the

basis of the spectral analysis, in particular by comparison with the spectra of unsubstituted phenanthrenes and azaphenanthrenes, to be the ones derived from the *cis* isomers in the case of both α -phenyl-2- and 4-styrylpyridine.

When samples of both *cis* and *trans* isomers were irradiated in *n*-hexane for different time intervals, and then spotted on TLC plates and observed under 366 nm light under which only the cyclized compounds display fluorescence, the following was observed: (a) on irradiation of the *cis* isomer, the fluorescent spot due to its cyclization product was first observed; only much later, when the

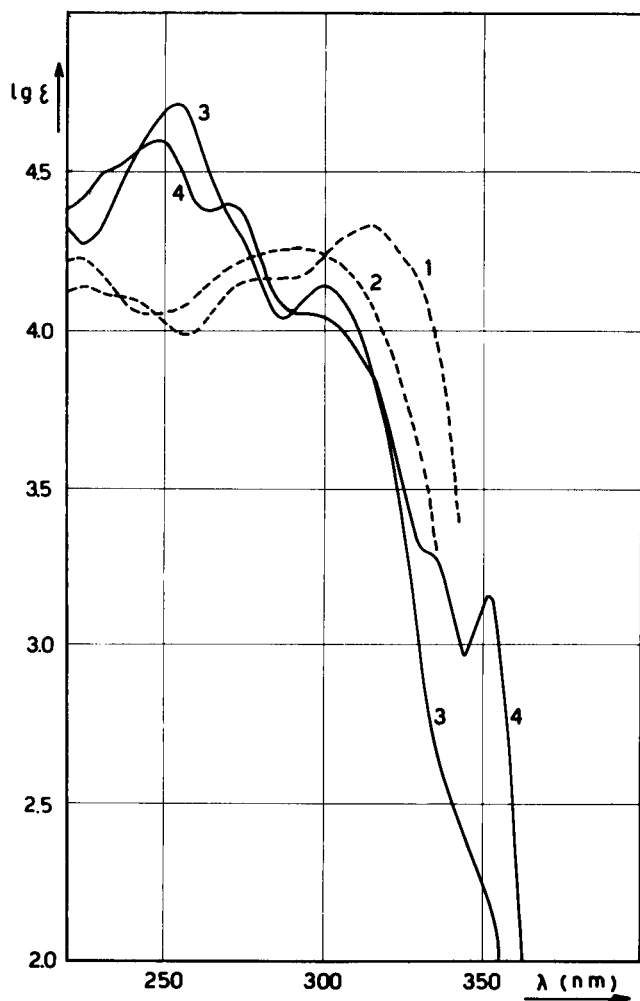


Figure 4. Absorption spectra of *trans* (curve 1) and *cis* (curve 2)- α -phenyl-2-styrylpyridine and of their photocyclization products, 10-(2-pyridyl)phenanthrene (curve 3) and 10-phenyl-1-azaphenanthrene (curve 4) in *n*-hexane.

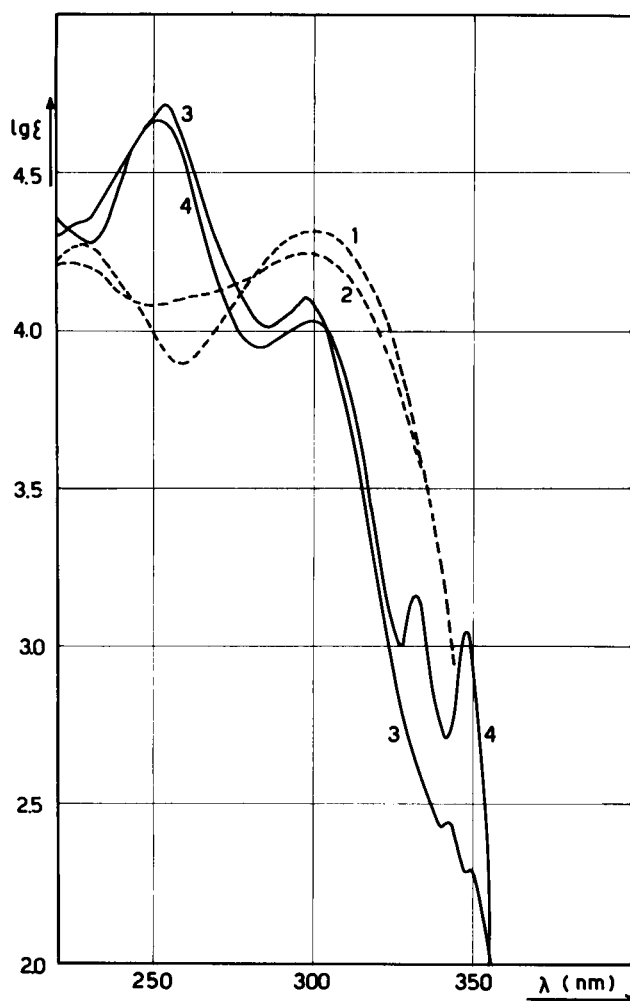


Figure 5. Absorption spectra of *trans* (curve 1) and *cis* (curve 2)- α -phenyl-4-styrylpyridine and of their photocyclization products, 10-(4-pyridyl)phenanthrene (curve 3) and 10-phenyl-3-azaphenanthrene (curve 4) in *n*-hexane.

conversion to *trans* became appreciable (as observed by its characteristic non-fluorescent spot), did the fluorescence of the pyridyl-substituted phenanthrene appear; (b) on irradiation of the *trans* isomer, on the other hand, the presence of the two fluorescent photoproducts appeared from the beginning of the irradiation, but no *cis* isomer was present in observable amounts.

This behaviour is understandable on the basis of a greater photocyclization rate of the *cis* isomer, which is in agreement with the predominance of the azaphenanthrene derived from the *cis* form in the preparative photochemical cyclization. This also indirectly confirms the *cis-trans* assignment reported before (16).

Quantum yields for these photoreactions were measured and the values are shown in Table 1. Owing to the similarity of the absorption spectra, the quantum yields of the photoisomerizations of α -phenyl-4-styrylpyridine were not obtained. It is to be noted that the overall photocyclization yields refer to both isomeric cyclized products derived from the corresponding *cis* and *trans* styrylpyridines which isomerize competitively. However, it is known from the preparative work that the azaphenanthrenes are the major products.

It is evident that α -phenyl substitution slows down both photoisomerization and photocyclization compared to the α -methyl-substituted as well as to the unsubstituted com-

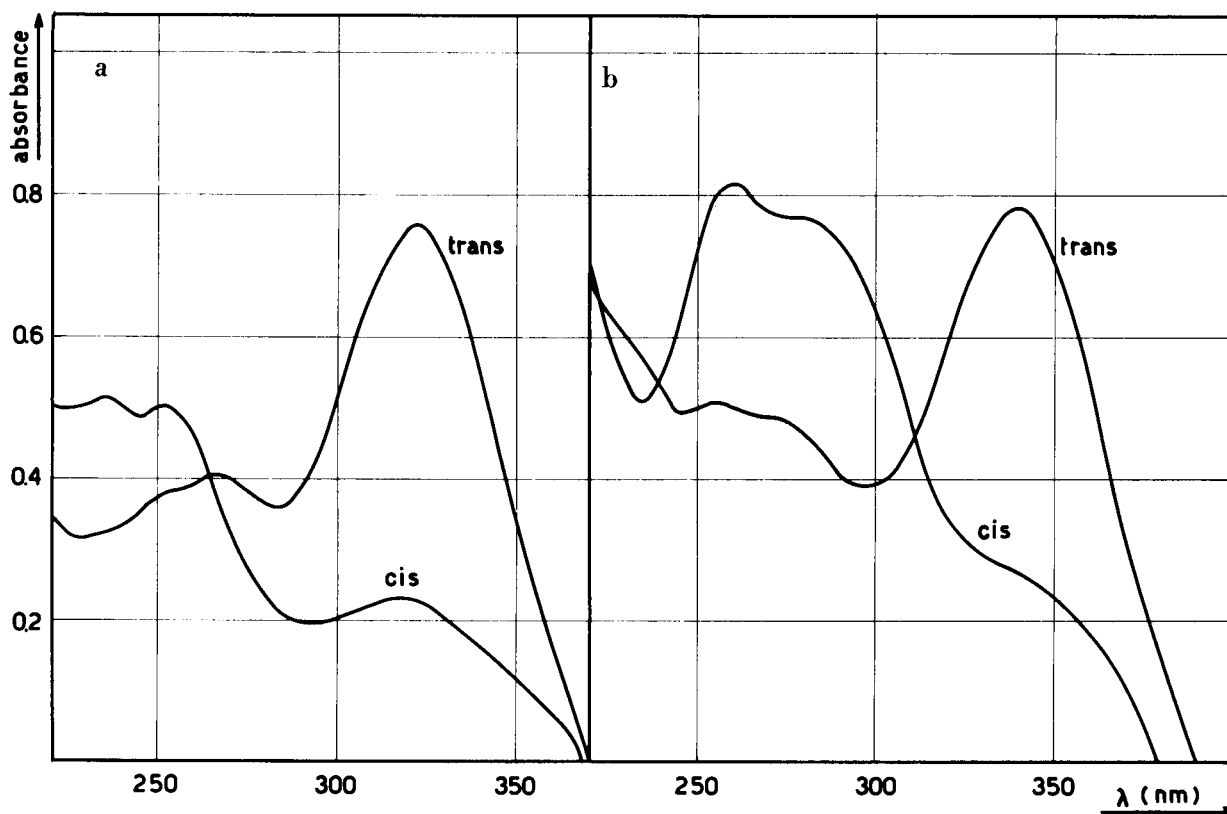


Figure 6. Absorption spectra of the geometrical isomers of α -methyl (curves a) and α -phenyl (curves b)-2-styrylpyridines (conc. = $4.45 \times 10^{-5} M$) in water-ethanol (5% of alcohol by volume) at $pH \approx 2$.

pounds. The data, in particular those for the 2-styrylpyridine derivatives, confirm that the *cis* isomer is the faster to photocyclize under our experimental conditions leading to phenyl-substituted azaphenanthrene, even though, at the beginning of the photoreaction, it tends to be converted into the *trans* form because of a high rate of *cis* \rightarrow *trans* photoisomerization.

EXPERIMENTAL

Spectra.

U.V. absorption spectra were recorded on Unicam SP500 single beam and on CF4 DR double beam spectrophotometers; N.M.R. spectra on a Varian A 56/60 spectrometer.

Chromatography.

Chromatographic analyses were performed by ascending T.L.C. (thin layer chromatography) on silica gel (thickness: 0.2μ). The eluents were: (a) butanol-acetone-water = 80:20:20; (b) butanol-acetic acid = 80:20; (c) chloroform-acetone-acetic acid = 60:30:10; (d) ethyl ether-dimethyl-formamide = 99:1; (e) ethyl ether-petroleum ether = 50:50.

In the preparative experiments alumina and silica gel (Merck

1097 and 7734) columns were used. The eluents were; petroleum ether-benzene in variable ratios; benzene; ethanol; chloroform. Molecular Weights.

The molecular weights were estimated by a Mecrolab V.P.D. Model 301 A.

Light Sources.

Mercury vapour lamps were used: (a) for analytical purposes, low pressure "Minerallight" for 254 nm and Osram "HQV 125 W.", for 366 nm light; (b) for preparative photochemistry, low pressure Hanovia immersion lamp TNK 6/20 and high pressure 1000 W Hanovia immersion lamp Q 1200/PL 357.

Melting Points.

Melting points were determined on a Kofler hot stage apparatus.

Preparation of *cis* α -Methyl Styrylpyridines.

Two methods were employed. The first one involved the irradiation of an aqueous solution of *trans*-styrylpyridine hydrochloride. These conditions appreciably slow down the photocyclization reaction (2).

The second one involved the irradiation of the free base in benzene solution in order to avoid the dimerization to cyclobutane derivatives (8,11). In both cases, the Hanovia Q 1200 lamp

with a Pyrex filter ($\lambda \geq 310$ nm) was used, so that the light was mainly absorbed by the *trans* isomer and the photoreactions of the *cis* isomer were prevented.

The procedure for the separation of the photoproducts in the mixture obtained by irradiation and the yields of the *cis* isomer were essentially the same with both methods employed for the 2 and 4-styrylpyridine derivatives. We report, as an example, the procedure for α -methyl-2-styrylpyridine hydrochloride. For the characteristic parameters, see Table 2.

cis- α -Methyl-2-styrylpyridine.

Ten g. of *trans* product, prepared according to Phillips (6) and purified in order to get a product with melting point 42° , were dissolved in 36% hydrochloric acid (100 ml.) and diluted to 2000 ml. with distilled water. After an 8-hour irradiation in the presence of air, the solution was neutralized and the product was fractionally extracted with 400 ml. of benzene. Drying the benzene solution yielded 9.4 g. of product. Repeated crystallizations from *n*-hexane gave 1.1 g. of chromatographically and analytically pure *cis* compound (see Table 2). The mother liquors were collected and chromatographed with an alumina column (\varnothing 5 cm., length 50 cm.), using petroleum ether and petroleum ether-benzene mixtures as eluents. In this way, 1.7 g. of additional pure *cis* compound were isolated. Finally, 6.5 g. remained which were not further purified. The molecular weight of the isolated product was in good agreement with the expected value, thus ruling out the formation of a dimer. The isolated compound was further characterized by photocyclization under the 254 nm light of a sample of the *trans* compound and of a sample of the *cis* compound. In both cases, the same azaphenanthrene as described by Timmons (10) (m.p. 100° - 101°) was obtained.

Preparation of α -Phenyl-2-styrylpyridine.

2-Benzylpyridine (25 g., 0.149 mole) was treated with 31.4 g. (0.296 mole) of benzaldehyde, and 15.1 g. (0.148 mole) of acetic anhydride. The mixture was refluxed at about 140° for 48 hours. The excess benzaldehyde was removed by distillation in a stream of vapour and the compound was extracted from oil suspension with 300 ml. of chloroform in three fractions. The chloroform solution was dried on sodium sulfate, filtered, and the solvent was removed by distillation. The product was collected as a yellow oil by distillation under 0.5 mm Hg at 175 - 185° . In this way, 35 g. of product were recovered. The elemental analysis (see Table 3) and the molecular weight determination gave the expected results.

Two products were found to be present by chromatographic analysis (T.L.C.). This was ascribed to the presence of both the *trans* and *cis* isomers in the distillate. Moreover only the prevailing isomer (*trans*) was isolated. The *cis* isomer was isolated after enrichment of the mixture by photochemical *trans* \rightarrow *cis* isomerization.

A similar procedure was followed for the 4-styrylpyridine derivative (see Table 3).

Cyclization of *trans*- α -Phenyl-2-styrylpyridine.

(a) In the Presence of Oxygen ($c_{trans} \approx 2.10^{-3} M$).

α -Phenyl-2-styrylpyridine (0.3 g.) was dissolved in 500 ml. of *n*-hexane within a special apparatus equipped with a refrigerating jacket, a magnetic stirrer, and tubes for gas inlet or outlet with airtight closure. The solution was bubbled with oxygen previously passed through a pre-saturator, and irradiated by the low pressure lamp for 50 hours. The progress of the reaction was followed by T.L.C. and U.V. spectroscopy.

The reaction was assumed to be over on the basis of the formation of fluorescent chromatographic spots and of the attainment of an U.V. spectrum analogous to the one of the cyclized compounds. The product was dried and taken up with petroleum ether, passed through an alumina column (3 x 30 cm.). Petroleum ether, petroleum ether-benzene mixtures and 99% ethanol were used as eluents. The collected fractions involved decomposition products, *trans* and *cis* isomers, 10-phenyl-1-azaphenanthrene and 10-(2-pyridyl)-phenanthrene. The structure of the last two products was determined from N.M.R. spectra. The amount of 10-phenyl-1-azaphenanthrene, was 120 mg. (yield 40%; the yield of crude product was 65%). The amount of 10-(2-pyridyl)phenanthrene appeared to be very small (about 6% crude). Greater amounts of the two uncyclized isomers (90 mg., about 30%) were recovered.

(b) In the absence of Oxygen ($c_{trans} \approx 9.10^{-3} M$).

The procedure was the same as described above; however, highly purified nitrogen was flushed in the place of oxygen. The product (1.15 g.) was dissolved in 500 ml. of *n*-hexane. After 420 hours irradiation, the U.V. spectrum and T.L.C. showed that the reaction was far from complete.

The separation was achieved as in the preceding case. The total amount of the cyclization products was 150 mg. (yield 10-15%). The *cis* product (400 mg; m.p. 93 - 94° , theoretical values of the elemental analysis and molecular weight) and 400-450 mg. of liquid *trans* product were also obtained. After suitable chromatographic separations, 20 mg. of 10-(2-pyridyl)phenanthrene, m.p. 87 - 89° , were obtained.

(c) With Pyrex Filter ($\lambda \geq 310$ nm; $c_{trans} \approx 2.10^{-3} M$).

α -Phenyl-2-styrylpyridine (1.19 g.) was dissolved in 2.5 liters of benzene (similar behaviour was found in *n*-hexane) and irradiated for about 50 hours with the high pressure immersion lamp in the presence of oxygen. The effect of the excitation wavelength has been investigated since it can modify both the photostationary *cis-trans* composition (1) as well as the ratio of the two isomeric photocyclized products (1-2). The completeness of the reaction was checked by T.L.C. and by spectral analysis. In the subsequent chromatographic separation, 0.4 g. of 10-phenyl-1-azaphenanthrene (m.p. 114 - 115°) and 0.137 g. of the second cyclization product (m.p. 87 - 90°) were recovered. In this way, the yield of 10-(2-pyridyl)phenanthrene was noticeably increased, the ratio between the cyclic products being about 10:3.5 in favour of the azaphenanthrene. Similar results have been obtained for the 4-styrylpyridine derivative. Data are collected in Table 4.

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and 10-phenyl-3-azaphenanthrene in T.F.A. (where a better resolution is found) are 7.8 and 7.6, respectively, indicating the presence of a monosubstituted benzene nucleus (five equivalent protons). Furthermore, for 10-phenyl-3-azaphenanthrene in TFA, the signals at 8.6 (doublet) and 10.3 (singlet) were assigned to the protons in ortho to the heteroatom (positions 2 and 4). Should this compound contain a para-monosubstituted pyridine nucleus, these signals should be nearly coincident.

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(16) Prolonged irradiation of the spots with 254 nm light produces further photochemical reactions on the layers and in particular the appearance of the fluorescent phenanthrenic derivatives from the spots of *cis* and *trans* isomers.

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