

colorless needles of 1-acetoxy-2-benzimidazole (IX), mp 196–197° (yield quantitative).

Anal. Calcd for $C_{12}H_{12}N_2O_2$: N, 11.1. Found: N, 11.1.
IX when heated with water hydrolyzed back to VIII.

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Photochemical Methods in the Synthesis of Heterocyclic Compounds. I. Phenanthridizinium Perchlorates¹

R. E. DOOLITTLE AND C. K. BRADSHER

Department of Chemistry, Duke University, Durham, North Carolina

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Ultraviolet irradiation of solutions containing 1-styrylpyridinium salts and a small quantity of iodine effects cyclization and dehydrogenation to yield phenanthridizinium (benzo[*a*]quinolizinium) salts. Irradiation of suitably substituted 1-styrylpyridinium salts affords a practical synthetic route to phenanthridizinium cations substituted in either of the terminal rings.

The observation that the irradiation of stilbene with ultraviolet light in the presence of air or oxygen leads to the formation of phenanthrene² has prompted attempts to apply the photocyclization method to the synthesis of heterocyclic analogs of the phenanthrene system. Recently there have been reports of the synthesis of naphtho[2,1-*b*]thiophene from the cyclization of 2-styrylthiophene³ as well as of diaza- and azaphenanthrenes from azobenzene,⁴ stilbazoles,⁴ and Schiff bases.⁵

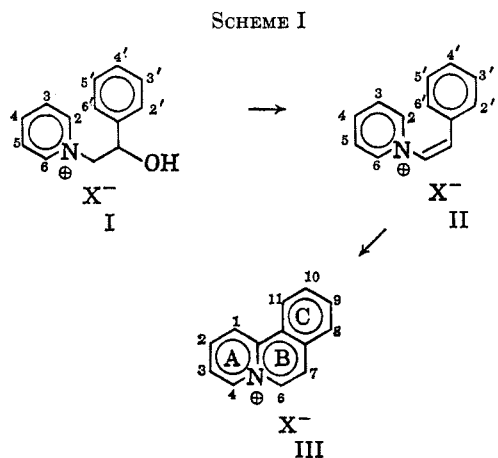
It has now been found that the photocyclization of 1-styrylpyridinium cation II (bromide or perchlorate) leads in 60% yield to the phenanthridizinium⁶ or 8*a*-azoniaphenanthrene⁷ cation (IIIa) (see Scheme I and

Table I). Best results for the cyclization were obtained by irradiating a well-stirred ethanol solution of the styryl salts (II) containing some iodine.²

TABLE I
PHENANTHRIDIZINIUM PERCHLORATES (III)
OBTAINED BY IRRADIATION

III	R	Yield, %	λ_{\max} , $m\mu$ (log ϵ) ^a
a	H	60	See ref 6
b	1,3-(Me) ₂	47	265 sh, 273 (4.42), 280 (4.43), 332 (3.79), 346 (4.09), 363 (4.24)
c	1,3-(Ph) ₂	50	255 sh, 275 sh, 293 (4.49), 360 (4.08), 375 (4.17)
d	8-Me	56	272 sh, 285 (4.47), 325 (3.79), 341 (3.98), 357 (4.08)
e	10-Me	66	363 (4.18), 275 sh, 285 (4.31), 329 (3.66), 344 (3.98), 361 (4.13)
f	8-OBz	43	260 sh, 271 sh, 281 (4.49), 324 (3.84), 339 (4.05), 355 (4.13)
g	10-Cl	60	250 sh, 265 sh, 280 (4.14), 330 (3.55), 345 (3.80), 363 (3.90)
h	8,9-(OBz) ₂	25	275 sh, 281 (4.61), 310 sh, 323 (3.96), 338 (4.16), 355 (4.23)
i	8,10-(OBz) ₂	50	283 (4.34), 303 (4.18), 327 (4.09), 345 (3.82), 361 (3.88)

^a Absorptions below 250 $m\mu$ have been omitted.



(1) This research was supported by a research grant (CA-05509) from the National Cancer Institute of the National Institutes of Health. This work has been made the subject of a preliminary communication: R. E. Doolittle and C. K. Bradsher, *Chem. Ind. (London)*, 1631 (1965).

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(6) (a) E. E. Glover and G. Jones, *J. Chem. Soc.*, 3021 (1958); (b) R. W. L. Kimber and J. C. Parham, *J. Org. Chem.*, **28**, 3205 (1963); (c) S. Akaboshi and T. Kato, *Yakugaku Zasshi*, **83**, 1067 (1963). Our sample was compared directly with IIIa obtained by the method of Kimber and Parham.

Several substituted styrylpyridinium salts were known previously, and more were prepared by dehydration of 1-(β -aryl- β -hydroxyethyl)pyridinium salts (I) in boiling benzoyl chloride.⁸ The β -hydroxyethyl salts (I) were prepared either by quaternization of a pyridine derivative by styrenebromohydrin^{8,9} or by condensation of a 1-methyl-⁸ or 1-phenacylpyridinium⁹ bromide with an appropriate aldehyde. The results obtained by irradiation of the styrylpyridinium salts are recorded in Table I. Substituted phenanthridizinium salts may be prepared with substituents in either of the terminal rings. The yields, except for that of 8,9-dibenzoxyphenanthridizinium cation, were of the order of 50%, although no effort was directed

(7) Nomenclature is based upon the 1957 report of the IUPAC Nomenclature Committee, *J. Am. Chem. Soc.*, **82**, 5545, 5572 (1960).

(8) L. C. King and W. B. Brownwell, *ibid.*, **72**, 2507 (1950).

(9) F. Kröhnke, *Ber.*, **68B**, 135 (1935), and references cited therein.

TABLE II
 NEW 1-(β -ARYL- β -HYDROXYETHYL)PYRIDINIUM BROMIDES (I)

Substituents	Procedure ^a	Yield, %	Mp, °C	Formula	C, %		H, %		N, %	
					Calcd	Found	Calcd	Found	Calcd	Found
3,5-(Me) ₂	A	65	228-229	C ₁₅ H ₁₈ BrNO	58.45	58.41	5.89	5.78	4.55	4.62
3,5-(Ph) ₂	A	44	216-218	C ₂₅ H ₂₂ BrNO	69.44	69.44	5.13	5.14	3.24	3.35
2',3'-(OMe) ₂	B	23	205-206	C ₁₅ H ₁₈ BrNO ₂	52.95	53.13	5.33	5.34	4.12	4.40
2,4'-(OMe) ₂	B	17	235-236	C ₁₅ H ₁₈ BrNO ₂	52.95	53.12	5.33	5.22	4.12	4.21

^a Procedure A involved the quaternization of the substituted pyridine with styrene bromohydrin [J. Read and W. G. Reid, *J. Chem. Soc.*, 1487 (1928)] as described in ref 8 and 9. Procedure B was the direct condensation of the appropriate benzaldehyde with 1-methylpyridinium bromide in the presence of piperidine as described by ref 8.

 TABLE III
 NEW 1-(β -STYRYL)PYRIDINIUM SALTS (II)

Substituents	Ref ^a	Yield, %	Mp, °C	X ⁻	Formula	C, %		H, %		N, %	
						Calcd	Found	Calcd	Found	Calcd	Found
3,5-(Me) ₂	b	57	232-234	Br	C ₁₅ H ₁₆ BrN · 0.5H ₂ O	60.19	60.56	5.72	5.93	4.71	4.51
3,5-(Ph) ₂	b	43	290-292	ClO ₄	C ₂₅ H ₂₀ ClNO ₄	69.20	68.96	4.65	4.68	3.32	3.10
2'-Me	c	3	192-193	Br	C ₁₄ H ₁₄ BrN	60.88	60.62	5.11	5.09	5.19	5.28
4'-Me	d	52	272-275	Br	C ₁₄ H ₁₄ BrN	60.88	60.89	5.11	5.18	5.19	5.19
2'-OBz	e,f	58	222-224	Br	C ₂₀ H ₁₈ BrNO ₂	62.84	62.61	4.22	4.39	3.67	3.80
2',3'-(OBz) ₂	b,e	34	239-241	Br	C ₂₇ H ₂₀ BrNO ₄	64.55	64.61	4.01	4.17	2.79	2.93
2',4'-(OBz) ₂	b,e	35 ^g	224-226	ClO ₄	C ₂₇ H ₂₀ ClNO ₈	62.13	62.03	3.86	3.97		

^a Reference to preparation of the required 1-(β -aryl- β -hydroxyethyl)pyridinium bromide. ^b Table II. ^c The carbinol (I) was not isolated in a pure state, but was dehydrated directly to the styryl salt (II). ^d F. Kröhnke and F. Fasold, *Ber.*, 67B, 656 (1934), and references cited therein. ^e The carbinol (I) was the corresponding methoxyl derivative. The methoxyl(s) underwent replacement by benzoxy(s) during the heating with benzoyl chloride. ^f See ref 9. ^g The yield is of the bromide, mp 226-228°.

 TABLE IV
 NEW PHENANTHRIDIZINIUM PERCHLORATES (III) BY PHOTOCYCLIZATION

Substituents ^a	Mp, °C	Formula	C, %		H, %		N, %	
			Calcd	Found	Calcd	Found	Calcd	Found
1,3-(Me) ₂	233-235	C ₁₅ H ₁₄ ClNO ₄	58.54	58.78	4.59	4.99	4.55	4.66
1,3-(Ph) ₂	307-308	C ₂₅ H ₁₈ ClNO ₄	69.53	69.17	4.20	4.56	3.24	3.15
8-Me	250-251	C ₁₄ H ₁₂ ClNO ₄	57.25	57.48	4.12	4.11		
10-Me	247-248 ^b	C ₁₄ H ₁₂ ClNO ₄	57.25	57.33	4.12	4.51	4.77	4.98
8-OBz	225-227	C ₂₀ H ₁₄ ClNO ₆	60.08	60.36	3.53	3.69	3.50	3.48
10-OBz	221-223	C ₂₀ H ₁₄ ClNO ₆	60.08	59.97	3.53	3.58	3.50	3.41
10-Cl ^c	265-266	C ₁₃ H ₈ Cl ₂ NO ₄	49.70	49.65	2.89	3.18	4.46	4.64
8,9-(OBz) ₂	257-258	C ₂₇ H ₁₈ ClNO ₈	62.37	62.82	3.49	3.70	2.70	2.96
8,10-(OBz) ₂ ^d	267-268	C ₂₇ H ₁₈ ClNO ₈	62.37	62.41	3.49	3.52	2.70	2.40

^a Except as noted, the styrylpyridinium bromides used in the irradiation experiments are described in Table III. ^b This compound was reported earlier^{6b} as melting at 231-233°. Since our preparation melted substantially higher, and since the method used earlier might lead to contamination of the product by a small amount of the 8 isomer, it seemed desirable to include the present data. ^c Obtained by irradiation of 1-(1'-chlorostyryl)pyridinium perchlorate [F. Kröhnke, J. Wolff, and G. Jentsch, *Ber.*, 84, 399 (1951)]. ^d By irradiation of perchlorate.

toward finding optimum reaction conditions for each cyclization.

In addition to the two styrylpyridinium salts symmetrically substituted in ring A [II, R = 3,5-(Me)₂ or 3,5-(Ph)₂] the styryl-3-methylpyridinium salt was irradiated. The product (56% yield) was shown to be a mixture by thin layer chromatography on alumina using ether-methanol as a solvent and iodine or Dragendorff's reagent to render the spots visible. The mixture had a composition approximately that expected for a methylphenanthridizinium salt, and examination of the nmr spectrum revealed two nearly equivalent peaks (approximate ratio 7:6) at τ 6.66 and 7.28, suggesting that there is little selectivity in the course of the reaction despite the great difference in the degree of steric hindrance to be expected between the 1- and 3-methyl derivatives. The nmr spectrum of 1,3-dimethylphenanthridizinium perchlorate (IIIb) showed two equal peaks at τ 6.70 and 7.31 due to the methyl protons.

One other observation of interest is that when 1-(β -aryl- β -hydroxyethyl)pyridinium salts, having one

or more methoxyl groups, are refluxed in benzoyl chloride they do not give the expected methoxy-styrylpyridinium salts but instead the corresponding benzoxystyryl salts.

The photocyclization of styrylpyridinium salts affords a route to phenanthridizinium salts difficult or impossible to prepare by reactions previously described.

Experimental Section

Elemental analyses were carried out by Ilse Beetz, Kronach, Germany, and by Galbraith Laboratories, Knoxville, Tenn. The melting points were determined in capillaries using the Mel-Temp apparatus. The ultraviolet absorption spectra were measured in 95% ethanol using a Cary Model 14 spectrophotometer. Nuclear magnetic resonance measurements were made with the Varian A-60 spectrometer using trifluoroacetic acid as the solvent and tetramethylsilane as an external standard.

All irradiations were carried out using a 250-w compact mercury vapor source, B.T.H. mazda type ME/D, with the glass lens removed.

1-(β -Aryl- β -hydroxyethyl)pyridinium Salts.—Data concerning the four new hydroxy salts (I) are summarized in Table II.

1-(2-Styryl)pyridinium salts were prepared by refluxing the corresponding 1-(β -aryl- β -hydroxyethyl)pyridinium bromides

with benzoyl chloride as recommended by King.⁸ The results are summarized in Table III.

Photocyclization of Styrylpyridinium Salts (II).—The usual procedure was to dissolve 0.50 g of the styrylpyridinium salt (II) in 200 ml of 95% ethanol in a 250-ml beaker, and then 25 mg of iodine was added. The top of the beaker was closed with aluminum foil and the solution was stirred magnetically while the solution was irradiated by a 250-w mercury lamp placed 20 cm from the side of the beaker. Progress of the reaction was followed by observing the ultraviolet absorption spectra of samples withdrawn at regular intervals.

Preliminary experiments done with the 1-styrylpyridinium cation revealed that the purity of the product was decreased if stirring was omitted, that distilled water was not quite so satisfactory a solvent for the irradiation (low solubility of iodine) as ethanol, that the perchlorate anion was as satisfactory as the bromide, and that the optimum reaction time was about 24 hr. Omission of iodine, but not the stirring, reduced the yield from

60 to 40% and gave a less pure product. While quantum yields were not determined, it was noted that decrease in intensity of radiation (operation of lamp at lower voltage or at greater distance from the solution) resulted in a marked decrease in the rate of cyclization.

After the irradiation was complete, the solution was concentrated and the salt (if not a perchlorate) was taken up in about 25 ml of water, filtered, and converted to a perchlorate by addition of perchloric acid. Methanol and methanol-ethyl acetate were used as solvents for crystallization. The yields represented in Table I are not optimum and in most cases are the result of a single experiment. New phenanthridizinium salts obtained by the photocyclization method are listed in Table IV.

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Aldehyde Synthesis. A Study of the Preparation of 9,10-Anthracenedicarboxaldehyde and Other Aromatic Dialdehydes

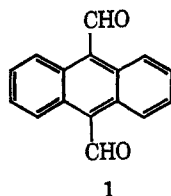
B. H. KLANDERMAN

Research Laboratories, Eastman Kodak Company, Rochester, New York 14650

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9,10-Anthracenedicarboxaldehyde can be conveniently prepared by the reaction of 9,10-bis(chloromethyl)anthracene in dimethyl sulfoxide with the sodium salt of 2-nitropropane. The role of dimethyl sulfoxide is shown to be that of a solvent only. Other methods for the preparation of 9,10-anthracenedicarboxaldehyde have been examined and shown to be of no value or inferior in some way to the above method. An unexpected product, 10-methyl-9-anthraldehyde, was formed as one of the products in the reaction of 9,10-bis(chloromethyl)anthracene with hot dimethyl sulfoxide. Tetramethylterephthaldialdehyde, 2,5-dimethylterephthaldialdehyde, and 1,5-naphthalenedicarboxaldehyde can also be easily prepared by the same procedure.

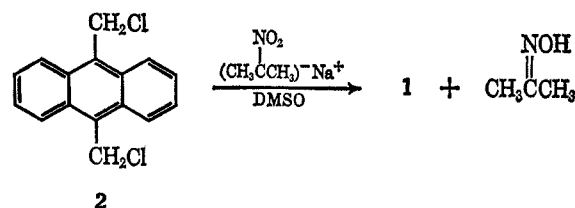
Aromatic dialdehydes, such as 9,10-anthracenedicarboxaldehyde (1), are potentially valuable synthetic intermediates. For the preparation of 1, no con-



venient, simple, and economical procedure is available. Two methods for the synthesis of 1 have been reported.¹ One method involves a low-yield, multi-step synthesis starting from anthraquinone and is obviously not practical. The other method employs the reaction of 9,10-dibromoanthracene with butyllithium to form the 9,10-dilithio derivative which gives aldehyde 1 upon treatment with dimethylformamide. This procedure is reasonable but is neither convenient nor economical.

Discussion

A simple, convenient, good-yield synthesis for aldehyde 1 has now been devised and shown to be general for three other aromatic dialdehydes. The reaction of a suspension of 9,10-bis(chloromethyl)anthracene (2) in dimethyl sulfoxide with an ethanolic solution of the sodium salt of 2-nitropropane leads to the formation of 1 in 70% yield. 9,10-Bis(chloromethyl)an-



thracene is readily prepared in good yield from anthracene *via* chloromethylation.²⁻⁶

Noteworthy features of this reaction are the following. (1) Dimethyl sulfoxide, as an additional solvent, is necessary for the reaction to occur. Aldehyde 1 cannot be prepared by the method of Hass and Bender⁷ which utilizes conditions similar to those mentioned without the use of dimethyl sulfoxide. (2) Dimethylformamide may also be employed as the reaction solvent, but yields are not so satisfactory (52%). (3) 2-Nitropropane is necessary for the reaction to occur. An experiment carried out without 2-nitropropane resulted in formation of 9,10-bis(ethoxymethyl)anthracene which obviously was formed from the reaction of sodium ethoxide with chloride 2. Furthermore, a vapor phase chromatographic analysis of a reaction mixture (using 2-nitropropane) confirmed

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