ml), and phosphorus pentachloride (18 g) was refluxed with stirring for 1 hr. The orange solution formed a nearly solid yellow mass on cooling to room temperature. Excess phosphorus oxychloride was removed by means of a rotary evaporator. The residue was cooled in an ice bath and crushed ice was added. When most of the ice had melted, the pale yellow solid was collected, washed with a little cold water, and taken up in 1 l. of vigorously boiling chloroform. A small amount of insoluble matter was removed by filtration. The chloroform solution was dried over anhydrous sodium sulfate and concentrated to dryness under reduced pressure: yield 5.15 g (90%) of XVIII, lemon yellow powder, mp 183–184° (lit.[7] mp 184°). Alternatively, XVIII could be purified effectively on a small scale by vacuum sublimation at 140° (0.05 mm). This compound appears to be highly unstable in the presence of traces of moisture. A carefully dried and spectroscopically pure sample of XVIII was observed to have generated hydrogen chloride (readily detectable by its odor) after storage for a few weeks in a screwcap bottle, and its infrared spectrum already indicated the presence of an appreciable quantity of XV at this time.

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Quinoxaline Derivatives. IX.[1a] An Unusual Chlorine Substitution in Quinoxaline N-Oxides. Its Scope and Limitations

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An oxygen function at C-3 in quinoxaline 1-oxides has been shown to control the nucleophilic chlorine substitution at C-6 observed[2] when these N-oxides are heated with acetyl chloride or ethanolic hydrogen chloride. In its absence the chlorine substitution (a) fails to take place as evidenced in the case of 2,3-diphenylquinoxaline 1-oxide (Ij) and 1,4-dioxide (IVj); (b) if it takes place as in the case of 2,3-dimethylquinoxaline 1-oxide (If) and 1,4-dioxide (IVf) is directed to the methyl groups; (c) takes place at a position adjacent to the N-oxide if it is previously unoccupied.

Newbold and Spring[3] observed that 3-ethoxy-2-methylquinoxaline 1-oxide (Ia) on treatment with boiling ethanolic hydrogen chloride instead of giving the expected 2-chloromethyl-3-hydroxyquinoxaline (IIb) gave 6-chloro-3-hydroxy-2-methylquinoxaline (IIIc). Similarly Clark-Lewis and Katekar[4] confirmed the observation of Usherwood and Whiteley[5] that 3,4-dihydro-4-methyl-2-(N-methyl-N-phenylcarbamoyl)-3-oxoquinoxaline 1-oxide (V) on reaction with ethanolic hydrogen chloride also gave a compound with chlorine substituted on the benzene ring. Clark-Lewis, *et al.*, deduced the structure of this chloro compound as VI. For the mechanism of this unusual chlorine substitution, the latter considered the protonated form[4,6] of the N-oxide responsible for the nucleophilic attack of the chloride anion on the benzene ring of the quinoxaline moiety. In support they have drawn an analogy between their mechanism[4] of this reaction and that of the mechanism of the formation of *p*-chloroaniline from phenylhydroxylamine as proposed by Ingold.[7]

(1) (a) Part VIII: Y. Ahmad, M. S. Habib, M. Iqbal, M. I. Qureshi, and Ziauddin. *Can. J. Chem.*, **43**, 3424 (1965). (b) To whom inquiries should be addressed. (c) Burroughs Wellcome and Co. (Pakistan) Ltd., D/43 S.I.T.E., Karachi.

(2) Y. Ahmad, M. S. Habib, Ziauddin, and N. Bashir, *Bull. Chem. Soc. Japan*, **38**, 1953 (1965).

(3) G. T. Newbold and F. S. Spring, *J. Chem. Soc.*, 519 (1948); W. Dawson, G. T. Newbold, and F. S. Spring, *ibid.*, 2579 (1949).

(4) J. W. Clark-Lewis and G. F. Katekar, *ibid.*, 2825 (1959).

(5) E. H. Usherwood and M. A. Whitely, *ibid.*, **123**, 1069 (1923).

(6) Y. Ahmad, M. S. Habib, M. Iqbal, M. I. Qureshi, and Ziauddin, *Bull. Chem. Soc. Japan*, **38**, 1659 (1965).

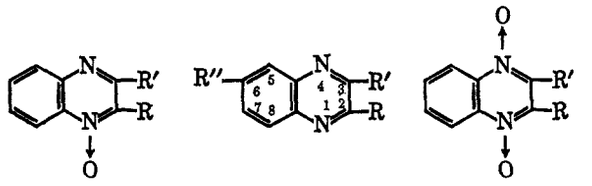
(7) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Bell, London, 1953, p 621.

In part VI[2] of this series, it has been shown that a large number of quinoxaline N-oxides bearing an aryl substituent at C-2 and a hydroxy group at C-3 undergo chlorination at position 6, on treatment with ethanolic hydrogen chloride (or acetyl chloride). A mechanism[2] has been proposed which envisages that attack of the reagent on the oxygen function at C-3 (probably augmented by the protonation or acylation of the N-oxide function) directs the nucleophilic attack of the chloride anion to position 6 of the quinoxaline. This mechanism fully and satisfactorily accounts[3,4] for the observations of Newbold, *et al.*, and Clark-Lewis, *et al.*, cited above.

In the present investigation the scope of this mechanism has been examined in further detail, and its generality has been established.

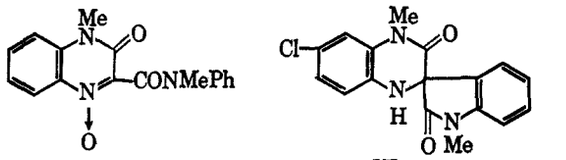
2-Phenylquinoline 1-oxide (VII), 2,3-diphenylquinoxaline 1-oxide (Ij), and the 1,4-dioxide IVj, all failed to react with acetyl chloride or ethanolic hydrogen chloride. Even when these reactions were carried out in sealed tubes at 100° for 24 hr, the starting materials in each case were recovered unchanged. This indicated that the N-oxides of these heterocycles in their protonated (or acylated) forms alone were unable to undergo the type of nucleophilic chlorination discussed above.

3-Phenylquinoxaline 1-oxide (Ik), when heated under reflux with acetyl chloride, gave a chlorine-substituted derivative, which was hydrolyzed with alkali to 3-hydroxy-2-phenylquinoxaline (IIq), indicating that the chloro compound formed in this reaction must have been 3-chloro-2-phenylquinoxaline

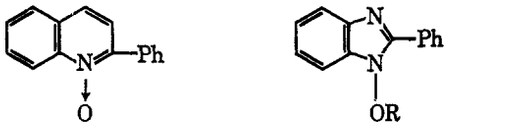


I II, R″ = H III, R″ = Cl IV

	R	R′		R	R′
a	Me	OEt	i	CO_2H	CO_2H
b	CH_2Cl	OH	j	Ph	Ph
c	Me	OH	k	H	Ph
d	CH_2Cl	Me	m	Cl	Ph
e	CH_2OH	Me	n	OH	Ph
f	Me	Me	p	Ph	Cl
g	CH_2Cl	CH_2Cl	q	Ph	OH
h	CH_2OH	CH_2OH	r	Me	CH_2Cl



V VI



VII VIII, R = H IX, R = Ac

(IIp). Similarly 2-phenylquinoxaline 1,4-dioxide (IVk) with acetyl chloride gave 3-chloro-2-phenyl quinoxaline 1-oxide (Ip); as on hydrolysis the latter compound gave a chlorine free compound identical with 3-hydroxy-2-phenylquinoxaline 1-oxide (Iq). An authentic synthesis of Iq has already been reported[8] from this laboratory. 3-Chloro-2-phenylquinoxaline 1-oxide (Ip) was recovered unchanged when heated with acetyl chloride (or ethanolic hydrogen chloride) in a sealed tube at 100° for 24 hr. This indicated that in this reaction even the presence of a strongly electronegative chloro group at C-3 of the quinoxaline N-oxide failed to create favorable conditions for the nucleophilic chlorine substitution to take place at C-6 or elsewhere in the molecule.

2,3-Dimethylquinoxaline 1-oxide (If) (which is an analog of Newbold and Spring's quinoxaline derivative Ia, in which the ethoxy group at position 3 has been replaced by a methyl group), when heated with acetyl chloride, gave a chlorine-substituted quinoxaline which was different from 6-chloro-2,3-dimethylquinoxaline[9] (IIIf). It was shown that the chlorine in this case had substituted a hydrogen atom in one of the methyl groups, as hydrolysis of this compound with alkali gave 2-hydroxymethyl-3-methylquinoxaline (IIe). An authentic sample of IIe, for comparison, was obtained by the interaction of 2,3-dimethylquinoxaline 1-oxide (If) with acetic anhydride, and subsequent hydrolysis *in situ* of the expected acetoxy intermediate (IIe, CH_2OAc for CH_2OH). Similarly when 2,3-dimethylquinoxaline 1,4-dioxide (IVf) was slowly added to an excess of acetyl chloride maintained at 0°, a solid X separated out, which dissolved when the mixture was heated under reflux; removal of the solvent gave a solid, which was purified through chromatography over alumina and was identified as 2,3-di(chloromethyl)-quinoxaline (IIg). The structure IIg for this chloro-compound was confirmed by hydrolysis with alkali to give 2,3-di(hydroxymethyl) quinoxaline (IIh). An authentic specimen of IIh was obtained by heating 2,3-dimethylquinoxaline 1,4-dioxide (IVf) with acetic anhydride, and subsequent hydrolysis *in situ* of the expected diacetoxy derivative (IIh, CH_2OAc for CH_2OH). 2,3-Di(hydroxymethyl)quinoxaline (IIh), obtained by either of the above methods, on oxidation with hydrogen peroxide in aqueous alkali was converted to quinoxaline-2,3-dicarboxylic acid (IIi), an authentic sample[10] of which for comparison was obtained by the condensation of sodium dihydroxytartrate with *o*-phenylenediamine. This clearly established that in either of the above reactions the chloro or acetoxy substituents had not entered the benzene portion of the quinoxaline derivatives. The elementary analysis of the compound X (see above) agreed well with that of 3-chloromethyl-2-methylquinoxaline 1-oxide (Ir), and it was assigned this structure on the evidence that when heated with acetyl chloride it gave 2,3-di(chloromethyl)quinoxaline (IIg).

The above investigation further supports the hypothesis put forward in earlier papers[2,6] that the presence of an oxygen function at C-3 in quinoxaline 1-oxides seems to be essential for the observed nucleophilic chlorination at C-6. When the quinoxaline N-oxides bear methyl groups at both the positions 2 and 3, the nucleophilic chlorination still takes place but in this case the chlorine enters the methyl groups. In case positions 2 and 3 are occupied by two phenyl groups, or a chloro and a phenyl group, no reaction takes place. When C-2 is unsubstituted and position 3 bears a phenyl group, chlorine enters the 2 position.

1-Hydroxy-2-phenylbenzimidazole[11] (VIII) (essentially 3-hydroxy-2-phenylquinoxaline 1-oxide devoid of its carbonyl at position 3), which possesses all the structural features necessary for the Ingold rearrangement[7] (phenylhydroxylamine → *p*-chloroaniline), when heated with acetyl chloride failed to give a chlorine-substituted derivative and instead gave an N-acetoxy compound IX, which with water alone was hydrolyzed back to VIII. This observation appears to invalidate Clarke-Lewis's suggestion[4] and further emphasizes the necessity of an oxygen function at position 3 of the quinoxaline 1-oxides for this type of chlorination to take place.

Experimental Section[12]

Materials.—2,3-Dimethylquinoxaline 1-oxide (If), 2,3-diphenylquinoxaline 1-oxide (Ij), and 1,4-dioxide (IVj) were prepared by the reported[9] methods.

1-Phenylquinoline 1-oxide (VII).—A mixture of 2-phenylquinolone[13] (5 g), glacial acetic acid (40 ml), and 30% hydrogen peroxide (10 ml) was heated under reflux for 4 hr. An additional amount of hydrogen peroxide (5 ml) and acetic acid (5 ml) was added after every hour. The mixture was reduced to 25-ml volume under vacuum in a rotary film evaporator and then poured on ice.

(8) Y. Ahmad, M. S. Habib, Ziauddin, and N. Bashir, *Tetrahedron*, **21**, 861 (1965).

(9) J. K. Landquist and G. J. Stacey, *J. Chem. Soc.*, 2822 (1953).

(10) F. D. Chattaway and W. G. Humphery, *ibid.*, 645 (1929).

(11) G. W. Stacy, B. V. Ettling and A. J. Papa, *J. Org. Chem.*, **29**, 1537 (1964).

(12) All melting points are uncorrected and were determined on Gallenkamp MF 370 melting point apparatus. Infrared spectra were measured in Nujol mull using a Perkin-Elmer Model 137B. The petroleum ether used had bp 60–80°.

(13) R. J. W. Le Fevre and J. Pearson, *J. Chem. Soc.*, 2807 (1932).

The precipitate was collected and the filtrate after neutralization with 10% sodium hydroxide was extracted with benzene. The benzene extract was dried (Na_2SO_4) and evaporated to dryness under reduced pressure. The total solid (5 g) when crystallized from petroleum ether, gave pale yellow needles of the 1-oxide (VII), mp 135–136°; Risaliti[14] recorded mp 144°.

Anal. Calcd for $C_{15}H_{11}NO$: C, 81.4; H, 5.0. Found: C, 81.2; H, 4.9.

2,3-Dimethylquinoxaline 1,4-Dioxide (IVf) (*cf.* **Landquist and Stacey**[9]).—By a similar procedure 2,3-dimethylquinoxaline (IIf) (5 g) gave the 1,4-dioxide (IVf) (3.5 g) which crystallized from benzene as yellow needles, mp 192–193° (lit.[9] mp 189–190°).

Anal. Calcd for $C_{10}H_{10}N_2O_2$: C, 63.15; H, 5.3; N, 14.7. Found: C, 62.2; H, 5.0; N, 14.8.

2-Phenylquinoxaline 1,4-Dioxide (IVk).—To a mixture of 2-phenylquinoxaline 4-oxide[9] (Ik) (8 g) and anhydrous formic acid (75 ml) was added slowly 30% hydrogen peroxide (30 ml). After controlling the initial exothermic reaction with cooling, the mixture was heated at 50° for 72 hr. An additional amount of hydrogen peroxide (15 ml) and formic acid (15 ml) was added after 24 and 48 hr. The mixture was reduced under vacuum to 40-ml volume, poured on ice, and neutralized with sodium hydroxide. The precipitated product was crystallized from ethanol to give 4.6 g of lemon yellow needles of the dioxide (Vk), mp 202–203. This was identical (infrared spectrum and mixture melting point) with the compound prepared by the method of Landquist and Stacey.

Treatment of N-Oxides with Acetyl Chloride or Ethanolic Hydrogen Chloride.—The following procedure (designated as procedure A) was followed for the isolation of the product in all cases of the interaction of the N-oxides with acetyl chloride described below. Similarly the procedure for isolation of the product of hydrolysis of chloro compound with aqueous ethanolic NaOH is designated as procedure B.

3-Chloro-2-Phenylquinoxaline 1-Oxide (Ip).—2-Phenylquinoxaline 1,4-dioxide (IVk) (2.0 g) was heated under reflux with acetyl chloride (25 ml) for 6 hr and acetyl chloride was removed under vacuum. The residue was treated with water and chilled overnight. The solid was collected, washed with water, and crystallized from ethanol as white microneedles of the chloro N-oxide (Ip), mp 126–127° (yield 78%).

Anal. Calcd for $C_{14}H_9ClN_2O$: C, 65.5; H, 3.5; Cl, 13.8; N, 10.9. Found: C, 65.1; H, 3.15; Cl, 13.8; N, 10.8.

The chloro compound (Ip) was recovered unchanged when heated with acetyl chloride in a sealed tube at 100° for 24 hr.

Ip (1.2 g) in ethanol (15 ml) was heated under reflux with 30% NaOH (15 ml) for 4 hr. Acidification after removal of alcohol gave a product which solidified on being chilled overnight (procedure B). The solid on crystallization from ethanol afforded yellow needles of 3-hydroxy-2-phenylquinoxaline 1-oxide (Ig), mp 305–306° (yield 64%).

Anal. Calcd for $C_{14}H_{10}N_2O_2$: N, 11.8. Found: N, 11.4.

This product of hydrolysis of Ip was identical (infrared spectrum and mixture melting point) with a sample[8] prepared earlier through an unambiguous route. This confirmed the constitution of Ip described above. Hayashi, *et al.*,[15] obtained Ip by the action of SO_2Cl_2 on IVk and gave its melting point as 126°.

3-Chloro-2-Phenylquinoxaline (IIp)—3-Phenylquinoxaline 1-oxide[9] (Ik) (2.5 g) and acetyl chloride (30 ml) were heated in a sealed tube for 24 hr at 100° and the product, isolated according to procedure A, crystallized from ethanol as white needles of the chloroquinoxaline (IIp), mp 127–128° (yield 85%).

Anal. Calcd for $C_{14}H_9ClN_2$: C, 69.8; H, 3.7; Cl, 14.7; N, 11.6. Found: C, 69.6; H, 3.8; Cl, 14.7; N, 11.6.

Shiho and Tagami[16] who obtained IIp by the action of $POCl_3$ on IIq recorded for it mp 130°. Ik remained unchanged when it was heated with acetyl chloride merely under reflux.

Hydrolysis of IIp with alkali by procedure B afforded in 64% yield 3-hydroxy-2-phenylquinoxaline (IIq), yellow needles, mp 258–260°, identical (infrared spectrum and mixture melting point) with an authentic sample[8] prepared by the condensation of ethyl phenylglyoxalate with *o*-phenylenediamine.

3-Chloromethyl-2-methylquinoxaline (IId).—2,3-Dimethylquinoxaline 1-oxide[9] (If) with acetyl chloride under reflux for 4 hr by procedure A gave in 80% yield (colorless needles from petroleum ether) of chloromethylquinoxaline (IId), mp 126–127°.

Anal. Calcd for $C_{10}H_9ClN_2$: C, 62.3; H, 4.7; Cl, 18.4; N, 14.5. Found: C, 62.4; H, 4.5; Cl, 17.8; N, 14.4.

IId on hydrolysis with alkali (procedure B) gave a product, which was extracted from the alkaline mixture with benzene and obtained as a low melting solid after removal of the solvent. It crystallized (from benzene–petroleum ether) as brownish plates, mp 108–110°, and was identical (infrared spectrum and mixture melting point) with IIe, obtained (for comparison) as follows.

2-Hydroxymethyl-3-methylquinoxaline (IIe).—If (2 g) was heated under reflux with acetic anhydride (20 ml) for 6 hr and acetic anhydride was removed under reduced pressure. The residue was diluted with water, neutralized with $NaHCO_3$, and extracted with ether. Removal of ether from the dried (Na_2SO_4) solution left a dark brown solid, which crystallized from benzene–petroleum ether as plates of the hydroxymethylquinoxaline (IIe), mp 108–110° (yield 50%).

Anal. Calcd for $C_{10}H_1N_{02}O$: C, 68.95; H, 5.8; N, 16.1. Found: C, 70.4; H, 5.6; N, 15.9.

2,3-Di(chloromethyl)quinoxaline (IIg).—The di-N-oxide[9] (IVf) (4.0 g) was added portionwise to well-stirred acetyl chloride (100 ml) at 0°. After complete addition the mixture was left overnight at room temperature. A grayish white solid X (1.8 g; see below) which separated out was filtered off and the filterate was heated under reflux for 4 hr and acetyl chloride was removed by distillation. The residue was washed with cold water containing a little ammonia, and crystallized from petroleum ether as white microneedles of the dichloromethylquinoxaline (IIg), mp 151–152°.

Anal. Calcd for $C_{10}H_8Cl_2N_2$: C, 52.8; H, 3.5; Cl, 31.3; N, 12.3. Found: C, 53.3; H, 3.6; Cl, 31.1; N, 11.9.

This was the only product of reaction when the mixture obtained after the interaction of IVf with acetyl chloride was heated under reflux without separation of solid X and in that case IIg was obtained in a yield of 85%. The solid X on crystallization from ethanol separated as colorless microneedles, mp 181–182°, which analyzed for 3-chloromethyl-2-methylquinoxaline 1-oxide (Id).

Anal. Calcd for $C_{10}H_9ClN_2O$: C, 57.8; H, 4.3; Cl, 17.0; N, 13.4. Found: C, 57.65; H, 4.1; Cl, 16.9; N, 13.7.

The constitution Id was confirmed for solid X, as it dissolved in acetyl chloride on being heated under reflux and in about 4 hr was smoothly converted to IIg.

IIg on hydrolysis with alkali (procedure B) gave a product, which on crystallization from benzene (charcoal) separated as light brown needles of 2,3-di(hydroxymethyl)quinoxaline (IIh), mp 131–132°, identical (infrared spectrum and mixture melting point) with an authentic sample, obtained as follows.

2,3-Di(hydroxymethyl)quinoxaline (IIh).—The di-N-oxide (IVf) (3.0 g) was heated under reflux for 6 hr with acetic anhydride (25 ml) and the product (2.1 g) isolated as described in the case of IIe. The product was purified by chromatography over alumina. It eluted out with benzene and on crystallization from benzene was obtained as light brown needles of the di-(hydroxymethyl)quinoxaline (IIh), mp 132–133°.

Anal. Calcd for $C_{10}H_{10}N_2O_2$: C, 63.15; H, 5.3; N, 14.7. Found: C, 63.3; H, 5.2; N, 14.9.

Oxidation[17] **of 2,3-Di(hydroxymethyl)quinoxaline (IIh).**—A mixture of IIh (0.5 g) obtained above, water (10 ml), 10% aqueous sodium hydroxide (5 ml), and 30% hydrogen peroxide (2 ml) was vigorously shaken at room temperature for 4 hr, heated on water bath for 0.5 hr, and then filtered. The filtrate, after evaporation under reduced pressure to nearly half its volume, was acidified and left overnight in a cooler. The separated solid after crystallization from hot water gave pale yellow needles of quinoxaline-2,3-dicarboxylic acid, mp 190° dec, identical (infrared spectrum and mixture melting point) with a sample prepared by the condensation of sodium dihydroxytartrate with *o*-phenylenediamine.

Interaction of 1-hydroxy-2-phenylbenzimidazole (VIII) with Acetyl Chloride.—1-Hydroxy-2-phenylbenzimidazole[11] (VIII) (1.0 g) and acetyl chloride (20 ml) were heated under reflux for 6 hr and in another case in a sealed tube at 100° for 72 hr. In either case the residue, after removal of acetyl chloride, crystallized from benzene (containing a few drops of dry methanol) as

(14) A. Risaliti, *Ric. Sci.*, **24**, 2351 (1954).

(15) E. Hayashi, C. Iijima, and Y. Nagasawa, *Yakugaku Zasshi*, **84**, 163 (1964).

(16) D. Shiho and S. Tagami, *J. Amer. Chem. Soc.*, **82**, 4044 (1960).

(17) *Cf.* A. Müller and I. Varga, *Ber.*, **72**, 1993 (1939).

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

Anal. Calcd for $C_{15}H_{12}N_2O_2$: 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 Perchlorates[1]

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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 phenanthrene[2] 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-styrylthiophene[3] 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 phenanthridizinium[6] or 8a-azoniaphenanthrene[7] 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]

SCHEME I

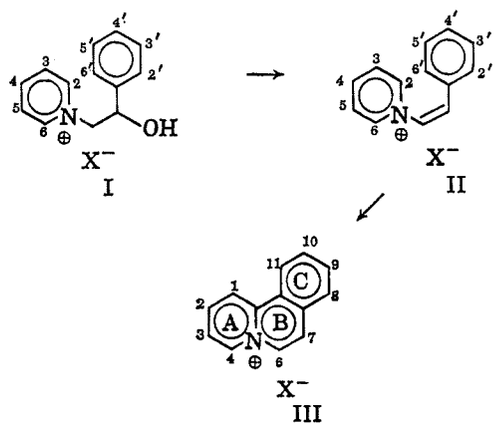

TABLE I

PHENANTHRIDIZINIUM PERCHLORATES (III) OBTAINED BY IRRADIATION

III	R	Yield, %	λ_{max}, mμ (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 mμ have been omitted.

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-phenacylpyridinium[9] bromide with an appropriate araldehyde. 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

(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).

(2) For a bibliography, see F. B. Mallory, C. S. Wood, and J. T. Gordon, *J. Am. Chem. Soc.*, **86**, 3094 (1964).

(3) W. Carruthers and H. N. M. Stewart, *Tetrahedron Letters*, 301 (1965).

(4) (a) P. Hugelshofer, J. Kolvada, and K. Schaffner, *Helv. Chim. Acta*, **43**, 1322 (1960); (b) G. E. Lewis, *Tetrahedron Letters*, **No. 9**, 12 (1960). (c) C. E. Loader, M. V. Sargent, and C. J. Timmons, *Chem. Commun.* (London), 127 (1965).

(5) M. P. Cava and R. H. Schlessinger, *Tetrahedron Letters*, 2109 (1964).

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