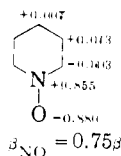


and takes place at the 3-position.²¹ The result agrees with Table III if it assumed that under the reaction conditions (fuming sulfuric acid), pyridine-1-oxide is present only in the salt form.

From the correlations with reactivity it can be concluded that the value of β_{NO} for pyridine-1-oxide is between 0.53β and 0.825β and the dipole moment calculations suggest a value nearer the higher of the two. By graphical means the charge distribution and atom localization energies may be determined for pyridine-1-oxide at $\beta_{NO} = 0.75\beta$, which is probably fairly near the true value.



Calculations.—The LCAO procedure described by Coulson²² was employed.

Pyridine.—The inductive effect of the nitrogen atom was taken into account by using for carbons 2 and 6, $\alpha_{C_{2,6}} = \alpha_C + 0.05\beta$; the other parameters were $\alpha_N = \alpha_C + 0.5\beta$ and $\beta_{CN} = \beta$. For the pyridinium ion the following substitutions were made, $\alpha_N = \alpha_C + 1.0\beta$ and $\alpha_{C_{2,6}} = \alpha_C + 0.1\beta$. The

- (21) H. S. Mosher and F. J. Welch, *THIS JOURNAL*, **77**, 2902 (1955).
 (22) Reference 4, pp. 238-256.

TABLE IV
 ATOM LOCALIZATION ENERGIES OF PYRIDINE-1-OXIDE
 ($\beta_{NO} = 0.75\beta$)

Position	A_0	A_1	A_2
2	2.36	2.42	2.48
3	2.58	2.53	2.50
4	2.44	2.47	2.46

energy levels for the molecular orbitals and the coefficients were determined by solution of the secular equations. The atom localization energies result by subtraction of the total energy of the π -electrons of pyridine from the π -electron energy of the "localized states." As an example, the localized state for electrophilic substitution at the 3-position is shown. For localization at each position a different set of secular equations was solved.



Pyridine-1-oxide.—The same procedure was followed as for pyridine. The parameters were: $\alpha_O = \alpha_C + 1.0\beta$, $\alpha_N = \alpha_C + 0.6\beta$ (0.6 instead of 0.5 because of the inductive effect of the oxygen atom), $\alpha_{C_{2,6}} = \alpha_C + 0.06\beta$, $\beta_{CN} = \beta$, $\beta_{NO} = 0.5$, 1.0 and 1.5. For the salt, $\alpha_O = \alpha_C + 1.5\beta$, $\alpha_N = \alpha_C + 0.65\beta$; $\alpha_{C_{2,6}} = \alpha_C + 0.065\beta$, $\beta_{NO} = 0.5\beta$.

NEW BRUNSWICK, N. J.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

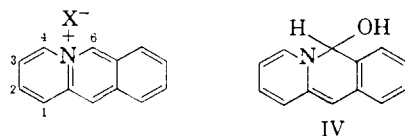
Acridizinium Ion Chemistry. III.¹ Reaction with Bases

BY C. K. BRADSHIER AND JAMES H. JONES²

RECEIVED OCTOBER 2, 1958

It has been demonstrated that phenylmagnesium bromide attacks acridizinium bromide at position 6 yielding a dihydro derivative (V) which can be dehydrogenated to a 6-phenylacridizinium salt. In basic media substituted acridizinium bromides as well as the parent compound react with potassium cyanide, phenylacetone, acetone and acetophenone. It is suggested that in these cases reaction occurs at position 6.

Since the first synthesis of acridizinium salts (I),³ papers have appeared concerning the photo-



- I, X = Br
 II, X = OC₆H₄(NO₂)₂
 III, X = OH

dimerization^{4a} of the system as well as its participation as the diene component in the Diels-Alder reaction.¹ To date it appears that no study has been made of the action of bases on the acridizinium ion or on the simple prototype of the series,

the quinolizinium ion.^{4b} Excellent models for such an investigation are provided by earlier work⁵⁻¹⁷ with pyridinium, quinolinium and isoquinolinium salts.

An aqueous solution of acridizinium bromide (I)

(4) (b) ADDED IN PROOF.—In a recent article (*J. Chem. Soc.*, 3067 (1958)) A. Richards and T. S. Stevens have studied the behavior of bases on both quinolizinium and acridizinium salts. It is interesting that under the conditions which they used they were unable to effect the condensation of acridizinium salts with "reactive methylene compounds" in the presence of bases.

(1) For the previous communication of this series see *THIS JOURNAL*, **80**, 933 (1958).

(2) Taken in part from a thesis submitted by James H. Jones in partial fulfillment of the requirements for the Ph.D. degree, Duke University, 1958.

(3) C. K. Bradshier and L. E. Beavers, *THIS JOURNAL*, **77**, 4812 (1955).

(4) (a) C. K. Bradshier, L. E. Beavers and J. H. Jones, *J. Org. Chem.*, **22**, 1740 (1957).

(5) J. G. Aston, *THIS JOURNAL*, **52**, 5254 (1930); **53**, 1448 (1931).

(6) A. Hantzsch and M. Kalb, *Ber.*, **32**, 3109 (1899).

(7) J. G. Aston and P. A. Lasselle, *THIS JOURNAL*, **56**, 426 (1934).

(8) J. G. Aston and C. W. Montgomery, *ibid.*, **53**, 4298 (1931).

(9) J. Meisenheimer and M. Schultze, *Ber.*, **56B**, 1353 (1923).

(10) J. Meisenheimer and E. Stotz and K. Bauer, *ibid.*, **58B**, 2320 (1925).

(11) W. Bradley and S. Jeffrie, *J. Chem. Soc.*, 2770 (1954).

(12) A. Kaufmann, *Ber.*, **51**, 116 (1918).

(13) N. J. Leonard and G. W. Leubner, *THIS JOURNAL*, **71**, 3405 (1949).

(14) N. J. Leonard and G. W. Leubner, *ibid.*, **71**, 3408 (1949).

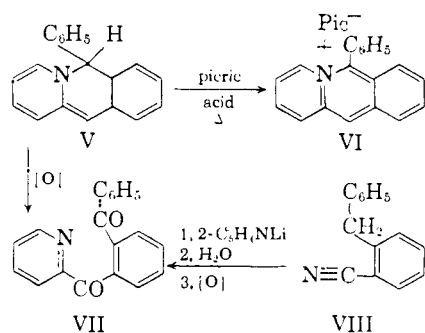
(15) N. J. Leonard, H. A. Dewalt, Jr., and G. W. Leubner, *ibid.*, **73**, 3325 (1951).

(16) N. J. Leonard and R. L. Foster, *ibid.*, **74**, 3671 (1952).

(17) N. J. Leonard and R. L. Foster, *ibid.*, **74**, 2110 (1952).

when made basic by addition of sodium hydroxide solution produced a red, water-insoluble precipitate. The precipitate appeared unstable, and was not obtained in a state of analytical purity. The freshly prepared precipitate dissolved in ether or benzene and the resulting solution yielded acridizinium picrate (II) upon addition of picric acid. Since it would be very remarkable if ionic acridizinium hydroxide (III) should prove to be soluble in benzene, the most likely explanation is that the pseudo base IV¹⁸ is formed instead. Aston and Montgomery⁸ pointed out that in aqueous solution aromatic quaternary hydroxides are largely ionic, and in equilibrium with only a small amount of the pseudo base, but if the pseudo base is sufficiently insoluble in water nearly all of the hydroxide can precipitate as the pseudo base.

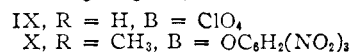
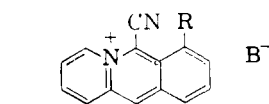
The nucleophilic attack of Grignard reagents on aromatic quaternary salts has been the subject of considerable study.⁹⁻¹¹ Just as had been observed with 1-methylquinolinium salts¹⁰ we found that acridizinium bromide (I) reacted with phenylmagnesium bromide to yield a dihydrobase (V) which on refluxing with ethanolic picric acid yielded the picrate of the aromatic quaternary salt VI. On oxidation, the dihydro base V yielded a color-



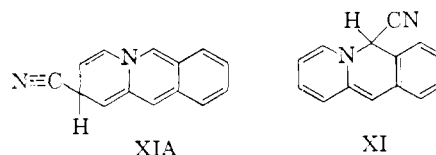
less crystalline compound having the composition expected for 2-(2-picolinyl)-benzophenone (VII). This structure was suggested further by the infrared absorption spectrum which showed the presence of the carbonyl group, but indicated that carboxyl was absent. The new diketone (VI) was synthesized from *o*-benzylbenzophenone (VIII) by reaction with *o*-pyridyllithium followed by oxidation. This demonstrates beyond any doubt that phenylmagnesium bromide attacks the acridizinium nucleus at position 6.

Kaufman¹² showed that 1-alkylquinolinium salts react with the cyanide ion to yield cyano dihydro bases. These bases may be aromatized by the action of iodine yielding 4-cyano-1-alkylquinolinium salts. When an aqueous solution of potassium cyanide is added to an aqueous solution of acridizinium or 7-methylacridizinium bromide a dark red precipitate is formed. The precipitate was taken up in methylene chloride and oxidized by boiling the solution with bromine. From the ultraviolet and infrared absorption spectra of the perchlorate salts, it is quite clear that cyanoacridizinium salts have been obtained. These we have formulated as the 6-cyanoacridizinium (IX) and

6-cyano-7-methylacridizinium salts. Although the reaction of quinolinium salts occurs at the *o*-position with Grignard reagents and *para* with the

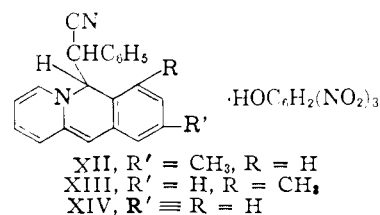


cyanide ion, it does not seem likely that the cyanide ion would add at position 2 of the acridizinium ion since the resulting dihydro compound XIA unlike that XI formed by addition at position 6, would have no benzenoid rings.



A final decision concerning the structure of these products as well as of those to be described subsequently will probably have to wait further advances in our knowledge concerning the synthesis of acridizinium derivatives.

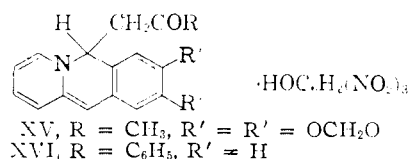
Leonard and Foster¹⁶ have shown that phenylacetonitrile will react with 1-methylquinolinium iodide in the presence of sodium ethoxide to yield 1-methyl-4-(α -cyanobenzyl)-1,4-dihydroquinoline. When a solution containing 9-methylacridizinium bromide and phenylacetonitrile in ethanol was made basic with sodium hydroxide and refluxed for two hours, an addition product was formed which was isolated as the picrate (XII). Unlike XI the dihydro base XII was not affected



by heating with bromine in an inert solvent. When the dihydro base XII was refluxed for 12 hours with ethanolic picric acid it was not dehydrogenated to yield a 6-substituted acridizinium derivative, but instead yielded some 9-methylacridizinium picrate. Leonard and Foster¹⁶ showed that 1-methyl-4-(α -cyanobenzyl)-1,4-dihydroquinoline was so sensitive to the action of picric acid that attempts to prepare a picrate led to the formation of 1-methylquinolinium picrate. With phenylacetonitrile, acridizinium bromide and 7-methylacridizinium bromide gave products believed to be XIV and XIII.

In basic acetone solution 8,9-methylenedioxyacridizinium bromide affords a mixture from which, by addition of picric acid, a compound believed to be 6-acetyl-8,9-methylenedioxy-5,6-dihydroacridizinium picrate (XV) was isolated in 33% yield. The addition of acetophenone to acridizinium bromide appears to give an analogous product (XVI). Under the same conditions, 9-methylacridizinium bromide or 8,9-methylenedioxyacridi-

(18) While this is considered the most likely structure for the pseudo base, at the present time no proof can be offered for its correctness.



zinium bromide yield products the composition of which indicates that *two* moles of acetophenone have reacted with each mole of the acridizinium halide. At present there is insufficient evidence available to make a decision concerning the structure of these two interesting derivatives.

Experimental¹⁹

Absorption Spectra.—The ultraviolet absorption spectra were measured in 95% ethanol solution using a Warren Spectracord spectrophotometer and 1-cm. quartz cells. The infrared spectra were obtained with a Perkin-Elmer model 21 spectrophotometer and were measured by the potassium bromide pellet technique.

4-Phenylbenzo[b]-4H-quinolizine (V).—To a solution containing slightly over two equivalents of phenylmagnesium bromide in 75 ml. of ether, 0.5 g. of acridizinium bromide³ was added and the mixture refluxed with rapid stirring for 1.5 hours. The inorganic salts were precipitated by addition of saturated ammonium chloride followed by sodium hydroxide solutions and the solid washed with an acetone-ether mixture until the wash solutions were colorless. The acetone-ether wash solution was concentrated to 50 ml. and a small amount of water added. On standing the solution afforded 0.25 g. (50.5%) of dark red needles, m.p. 110–115°. The melting point was not affected by recrystallization of the compound from dilute acetone.

Anal. Calcd. for C₁₉H₁₅N: C, 88.70; H, 5.88; N, 5.44. Found: C, 88.61; H, 5.93; N, 5.46.

6-Phenylacridizinium Picrate (VI).—By refluxing the free base V for several hours in alcoholic picric acid, brownish-yellow flakes were obtained, m.p. 188–190.5°.

Anal. Calcd. for C₂₅H₁₆N₄O₇·H₂O: C, 59.80; H, 3.61; N, 11.11. Found: C, 59.76; H, 3.55; N, 10.99.

2-(2-Picolonyl)-benzophenone (VII). (a) **By Oxidation of the Benzoquinolizine Base (V).**—To 0.3 g. of the base V in 100 ml. of acetone a 5% solution of potassium permanganate was added dropwise until the purple color persisted. The excess permanganate was destroyed by addition of alcohol, the manganese dioxide removed by filtration and washed with acetone. From the combined acetone solutions 0.06 g. of a brown solid melting at about 106° was obtained. On recrystallization from methanol it melted at 132–133.5°.

(b) **From *o*-Benzylbenzotrile (VIII).**—Butyllithium was prepared from 2.1 g. of butyl bromide. The ethereal solution was cooled to –60°, 3.3 g. of 2-bromopyridine in 50 ml. of dry ether was added, and the mixture maintained at –60° for a half-hour. A solution containing 4.0 g. of *o*-benzylbenzotrile²⁰ in ether was added, and the mixture allowed to come to room temperature over a period of 2 hours. The reaction mixture was poured into cold dilute hydrochloric acid, and the aqueous layer was separated. To the aqueous layer was added 50 ml. of concentrated hydrochloric acid and the solution was refluxed for one hour. The cooled solution was made basic and extracted with ether. The ethereal solution was concentrated under reduced pressure and the residue taken up in acetone. To the acetone solution a 5% solution of potassium permanganate was added until a purple color persisted. Excess permanganate was destroyed and the solution yielded 0.2 g. of a white solid, m.p. 132–133°. A mixed melting point with the preparation obtained by procedure a gave no depression and the infrared spectra of the two preparations were identical.

Anal. Calcd. for C₁₉H₁₅NO₂: C, 79.43; H, 4.56. Found: C, 79.13; H, 4.76.

(19) All melting points were taken on the Fisher-Johns apparatus and are uncorrected. All analyses were by Micro-Tech Laboratories, Skokie, Ill.

(20) C. K. Bradsher, *THIS JOURNAL*, **62**, 486 (1940).

6-Cyanoacridizinium Perchlorate (IX).—To a solution containing 1 g. of acridizinium bromide in 20 ml. of water an aqueous solution of potassium cyanide was added until there was no further precipitation of red solid. The solid was extracted by means of methylene chloride. The methylene chloride solution was boiled and to it a solution of bromine in methylene chloride was added until the precipitation of a yellow solid appeared complete. The solid was collected, dissolved in ethanol and perchloric acid added. Upon cooling the solution, 0.75 g. (64%) of dark yellow flakes separated, m.p. 250–255°. Further crystallization from ethanol did not alter the melting point.

The ultraviolet absorption spectra showed the following maxima: 364, 395, 408 and 432 m μ . Infrared absorption occurred at 2240 cm.⁻¹, a region assigned to the aromatic nitrile group.

Anal. Calcd. for C₁₄H₈ClN₂O₄: C, 55.18; H, 2.98. Found: C, 54.96; H, 2.81.

6-Cyano-7-methylacridizinium Picrate (X).—Starting with 0.5 g. of 7-methylacridizinium bromide³ the reactions were carried out as in the case of IX. The product obtained by addition of bromine was dissolved in ethanol-water and an ethanolic solution of picric acid added. This afforded 0.28 g. (35%) of orange needles, m.p. 192–200° dec. Recrystallization from ethanol afforded a product melting at 212–214° dec.

Anal. Calcd. for C₂₁H₁₃N₅O: C, 56.40; H, 2.93; N, 15.64. Found: C, 56.45; H, 3.23; N, 15.28.

6-(α -Phenyl- α -cyanomethyl)-5,6-dihydroacridizinium Picrate (XIII).—To a solution containing 0.5 g. of acridizinium bromide in 20 ml. of propyl alcohol, 0.5 g. of phenylacetone nitrile and 5 ml. of 1*N* sodium hydroxide was added. After the mixture had been heated on the steam-bath for 2 hours about 200 ml. of water was added and the red solid which separated was collected and dissolved in ethanol-water. Addition of ethanolic picric acid yielded 0.95 g. (51%) of a yellow crystalline solid, m.p. 148–150°. Recrystallization from ethanol gave an analytical sample, m.p. 151–152°. This compound shows infrared absorption at 2230 cm.⁻¹ (nitrile) and at 2070 and 2630 cm.⁻¹ (amine salt).

Anal. Calcd. for C₂₇H₁₉N₅O: C, 61.80; H, 3.64; N, 13.36. Found: C, 62.05; H, 3.97; N, 13.69.

6-(α -Phenyl- α -cyanomethyl)-7-methyl-5,6-dihydroacridizinium Picrate (XIV).—Using 0.5 g. of 7-methylacridizinium bromide³ instead of the parent compound and using the same procedure used in the preparation of XIII, the picrate crystallized as bright yellow needles, m.p. 175–178°, yield 0.45 g. (46%). The analytical sample was crystallized from ethanol, m.p. 176–178° (slight previous softening).

Anal. Calcd. for C₂₈H₂₁N₅O₇: C, 62.42; H, 3.92; N, 13.00. Found: C, 62.31; H, 4.14; N, 13.37.

6-(α -Phenyl- α -cyanomethyl)-9-methyl-5,6-dihydroacridizinium Picrate (XII).—In essentially the same way 9-methylacridizinium bromide was converted to the phenylacetone nitrile condensation product, isolated as the picrate, m.p. 175–180° dec. It was recrystallized from ethanol, m.p. 183–184° dec. The picrate showed infrared absorption at 2230 cm.⁻¹ (nitrile) and at 2070 and 2630 cm.⁻¹ (amine salt).

Anal. Calcd. for C₂₇H₁₉N₅O₇: C, 61.80; H, 3.64; N, 13.56. Found: C, 62.05; H, 3.95; N, 13.69.

It was found that the free base was not affected when treated with bromine in carbon tetrachloride solution.

6-Acetyl-8,9-methylenedioxy-5,6-dihydroacridizinium Picrate (XV).—One gram of 8,9-methylenedioxyacridizinium bromide²¹ was added to 40 ml. of acetone containing 1 ml. of 2*N* sodium hydroxide solution. The mixture was refluxed for 1.5 hours and then filtered. To the filtrate an ethanolic solution of picric acid was added. The solution was concentrated and diluted with water yielding 0.55 g. (33%) of a yellow powder, m.p. 195–200° dec. Recrystallization from ethanol afforded bright yellow granules, m.p. 205–208° dec.

Anal. Calcd. for C₂₃H₁₈N₄O₁₀: C, 54.10; H, 3.56; N, 11.00. Found: C, 53.89; H, 3.70; N, 10.95.

6-Phenacyl-5,6-dihydroacridizinium Picrate (XVI).—A mixture containing 0.5 ml. of acetophenone, 2.0 ml. of 1*N*

(21) C. K. Bradsher and J. H. Jones, *ibid.*, **79**, 6033 (1957).

sodium hydroxide and 0.5 g. of acridizinium bromide was refluxed for 2 hours. The red solution was poured into 75 ml. of cold water and extracted with carbon tetrachloride. A solution of bromine in carbon tetrachloride was added until precipitation of the salt appeared complete. The mixture was evaporated under reduced pressure and the residue dissolved in ethanol and treated with picric acid solution. The red solid was collected, m.p. 120–130°, yield 0.37 g. (37%). Recrystallization from ethanol gave a reddish-tan powder, m.p. 130–133°. This compound shows infrared absorption at 1682 cm^{-1} (phenyl ketone) and at 2080 and 2660 cm^{-1} (amine salt).

Anal. Calcd. for $\text{C}_{27}\text{H}_{20}\text{N}_4\text{O}_8 \cdot \frac{1}{2}\text{H}_2\text{O}$: C, 60.40; H, 3.93; N, 10.42. Found: C, 60.56; H, 3.77; N, 10.59.

Reaction of 9-Methylacridizinium Bromide with Acetophenone.—A mixture containing 0.5 g. of acetophenone, 0.5 g. of 9-methylacridizinium bromide and 5 ml. of 1 *N* sodium hydroxide solution in 25 ml. of propyl alcohol was refluxed for 2 hours and then diluted with water. The red oil which first formed solidified and was collected. It was immediately dissolved in a small quantity of ethanol and enough hydrochloric acid added to make the solution acidic and ethanolic picric acid was added. The crude precipitate weighed 0.41 g. (43%), m.p. 160–178°. The analytical sample crystallized from ethanol as yellow granules, m.p.

195–196°. This compound showed infrared absorption at 1682 cm^{-1} (phenyl ketone) and at 2080 and 2660 cm^{-1} (amine salt). The analysis indicated that the reaction of two moles of acetophenone per mole of 9-methylacridizinium bromide had taken place.

Anal. Calcd. for $\text{C}_{56}\text{H}_{40}\text{N}_4\text{O}_9$: C, 65.30; H, 4.57; N, 8.46. Found: C, 65.18; H, 4.54; N, 8.69.

Reaction of 8,9-Methylenedioxyacridizinium Bromide with Acetophenone.—A solution containing 0.5 g. of 8,9-methylenedioxyacridizinium bromide, 3 ml. of 1 *N* sodium hydroxide and 2 ml. of acetophenone in 20 ml. of ethanol was refluxed for 16 hours, after which it was poured into water and extracted with methylene chloride. The methylene chloride was evaporated and the residue converted to a picrate in ethanol solution; yield 0.46 g. (40%), m.p. 172–180°. The analytical sample crystallized from acetone-ethanol as dark yellow prisms, m.p. 200–202°.

This compound exhibits infrared absorption at 1682 cm^{-1} (phenyl ketone) and 2080 and 2660 cm^{-1} (amine salt). The analysis indicated the reaction of two moles of acetophenone per mole of the acridizinium derivative.

Anal. Calcd. for $\text{C}_{56}\text{H}_{37}\text{N}_4\text{O}_{11}$: C, 62.55; H, 3.94; N, 8.10. Found: C, 62.79; H, 4.12; N, 8.09.

DURIAM, N. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

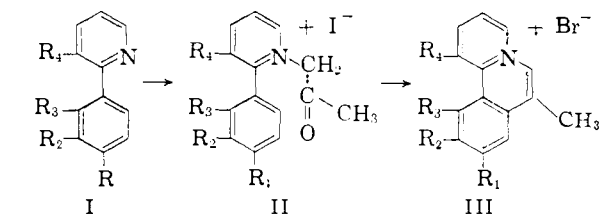
Aromatic Cyclodehydration. XXXVIII.^{1,2} Phenanthridizinium Derivatives with Substituents in the Terminal Rings

BY C. K. BRADSHER AND K. B. MOSER

RECEIVED OCTOBER 2, 1958

The method developed earlier for the synthesis of benzo[a]quinolizinium derivatives has been extended to the synthesis of fully aromatic benzo[a]quinolizinium salts having substituents in the terminal rings. The poor yield obtained in the cyclization of the 1-acetyl-2-(2-tolyl)-pyridinium salt (XI) has been attributed to steric interference with the achievement of coplanarity. The name phenanthridizinium has been proposed for the benzo[a]quinolizinium ion.

In an earlier communication³ it was shown that phenylpyridine (I) with iodoacetone yielded a quaternary cation (II) which, in the presence of boiling hydrobromic acid, afforded 7-methylphenanthridizinium salts⁴ (III).



$\text{R}_1 = \text{CH}_3$	IV	V	VI
$\text{R}_2 = \text{CH}_3$	VII	VIII	IX
$\text{R}_3 = \text{CH}_3$	X	XI	XII
$\text{R}_2 = \text{OCH}_3$	XIII	XIV	XV (picrate)
$\text{R}_4 = \text{OH}$	XVI	XVII (bromide)	XVIII

All R groups not otherwise specified are assumed to be hydrogen.

(1) For the previous communication of this series, see *J. Org. Chem.*, **23**, 430 (1958).

(2) Abstracted from part of a dissertation to be presented by K. B. Moser in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Duke University. This research was supported by a grant (NSF-G2364) from the National Science Foundation.

(3) C. K. Bradsher and L. E. Beavers, *THIS JOURNAL*, **77**, 453 (1955).

(4) The name phenanthridizinium as a substitute for benzo[a]quinolizinium ion offers the advantage of simplicity in the naming of derivatives, and is consistent with those of the quinolizinium and acridizinium ions. The numbering used is that recommended by *Chemical Abstracts*.

With the exception of the 1,2,3,4-tetracarboxyphenanthridizinium salts prepared by O. Diels and J. A. Harms (*Ann.* **525**, 73 (1936)), the only fully aromatic phenanthridizinium compounds appear to be those described in reference 3.

It was the purpose of the present work to learn whether this method was sufficiently general to allow the preparation of phenanthridizinium salts with substituents in the terminal rings. Of particular interest was the question whether substituents (R_3 and R_4) which might impede the achievement of coplanarity in the uncyclized salt would noticeably retard or even prevent the cyclization.

TABLE I
PHENANTHRIDIZINIUM SALTS

Substituent	Yield, % quaterni- zation	Cyclization time, hr.	Yield, % cyclization
$\text{R}_1 = \text{CH}_3$	65	50.5	71
$\text{R}_2 = \text{CH}_3$.. ^a	66	64 ^b
$\text{R}_3 = \text{Cl}$	85	50.5	9
$\text{R}_2 = \text{OCH}_3$	99	0.05	50
$\text{R}_4 = \text{OH}$	62	50	85

^a Yield not determined, but must be at least equal to over-all yield (64%). ^b Over-all yield from arylpyridine.

The salt XI formed by reaction of iodoacetone with 2-(2-tolyl)-pyridine (X) proved much more difficult to cyclize than did its isomers V and VIII. The 2-(2-tolyl)-pyridinium salt (XI) afforded only