1-Octanethiol (58.4 g, 0.4 mole) was added dropwise during 6 min to the above product which was still acid whereupon the temperature rose to 43°. After stirring for 1 hr, anhydrous sodium carbonate and a dropperful of concentrated NH_4OH were added. The vapor phase chromatograph indicated the product to be a mixture of 1-butanol and 1-[(1-octylthio)ethyl]-2-pyrrolidinone. Distillation of a 65-g sample through a flash still gave a forecut of butanol and 46.7 g (91%) of the octylthio compound, bp 144-146° (0.5 mm), $n^{25}D$ 1.4892.

Anal. Calcd for $C_{14}H_{27}NOS$: C, 65.30; H, 10.48. Found: C, 64.95; H, 10.15.

The retention time on the glpc was identical with that of the acid-catalyzed product of 1-octanethiol to **2**.

Attempted Reaction of N-Vinyl uccinimide with 1-Dodecanethiol.—A solution of 10.9 g (0.1 mole) N-vinylsuccinimide and 20.2 g (0.1 mole) of 1-dodecanethiol in 50 ml of methylene chloride at 21° was treated with 5 drops of concentrated sulfuric acid. After several minutes when no apparent reaction had occurred, and additional 5 drops of sulfuric acid was added. After standing for an additional 45 min the infrared spectrum of the solution was identical with the starting solution.

Registry No.—$C_9H_{14}N_2O_2$, 7594-58-3; $C_{12}H_{16}N_2O_3S$, 7594-59-4; $C_8H_{14}N_2O_3$, 7594-61-8; $C_9H_{14}N_2O_3$, 7594-62-9; $C_{13}H_{18}N_2O_4S$, 7594-63-0; $C_{13}H_{16}N_2O_3$, 7594-64-1; $C_{10}H_{16}N_2O_3$, 7594-60-7; $C_{12}H_{16}N_2O_4S$, 7594-66-3; $C_{15}H_{18}N_2O_4S_2$, 7594-67-4; $C_{18}H_{35}NOS$, 5681-84-5; $C_{14}H_{27}NOS$, 7594-69-6; $C_{18}H_{35}NO_2S$, 5681-87-8; $C_{12}H_{15}NO_2S$, 5681-86-7; $C_{14}H_{27}NO_2S$, 7594-72-1; $C_{21}H_{37}NO_2S$, 7594-73-2; $C_{16}H_{18}NO_2S_2Cl$, 7594-74-3; $C_{12}H_{23}NO_2S$, 5681-85-6; $C_{18}H_{38}S_2$, 7594-76-5.

Acknowledgment.—The authors are indebted to L. B. Westover and Dr. J. C. Gavan for infrared spectra and to Dr. J. P. Heeschen for nmr analyses. The elemental analyses were performed by Dow's Special Services Laboratory. Helpful discussions with Professors Martin Stiles and Jack Crump are acknowledged.

Acridizinium Ion Chemistry. VI.[1] Reaction with Bases. II[2]

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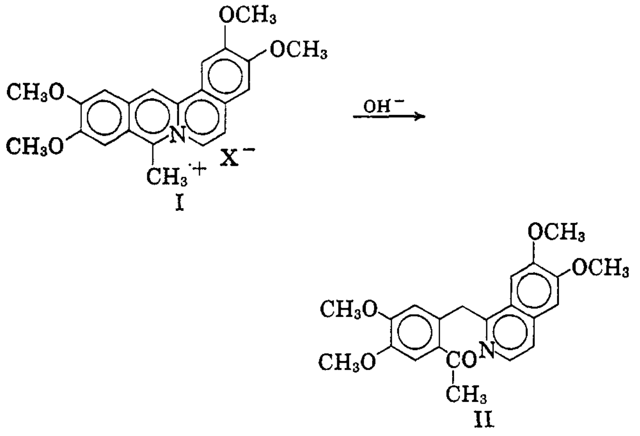
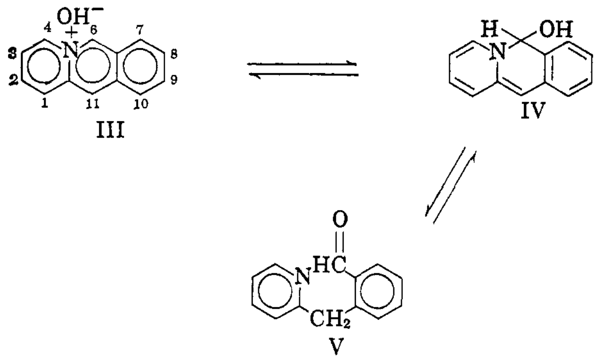
In basic solution the acridizinium ion under goes ring opening and can give base-catalyzed condensation of the type to be expected if 2-(2-formylbenzyl)pyridine were present. The easily prepared oxime of 2-(2-formylbenzyl)pyridine has been converted to 2-(2-cyanobenzyl)pyridine which proved to be a convenient starting material for the preparation of acridizinium and benzo[*b*]quinolizin-6-one derivatives.





In what was apparently the first paper to describe a quinolizinium derivative, Schneider and Schroeter[3] showed that coralyn (8-methyl-2,3,10,11-tetramethoxybenz[*a*]acridizinium, I) cation, in the presence of a base, underwent ring opening to afford a methyl ketone (II). By analogy it would be expected that addition of base to the acridizinium ion (III) might yield 2-(2-formylbenzyl)pyridine (V), probably *via* the pseudo-base (IV). Frost and Saylor[4] have invoked this equilibrium to explain the change in mode of polarographic reduction and the nature of the ultraviolet absorption spectrum in this system with increasing pH. It was reported earlier[5,6] that addition of base to an aqueous solution of acridizinium ion (III) leads to the precipitation of a red or brown powder. Although this powder has not yet been purified, evidence has been adduced (Experimental Section) which suggests that the material is a mixture of the aldehyde (V) and the pseudo-base (IV).

Evidence for the existence of the aldehyde (V) in basic alcohol solution was afforded by sodium borohydride reduction to afford the corresponding benzyl alcohol, 2-(2-hydroxymethylbenzyl)pyridine, which was isolated as the methoperchlorate. Proton magnetic resonance measurements support the assigned structure.

The most convincing chemical evidence for the presence of the formylbenzylpyridine (V) in an acridizinium solution that has been made basic was afforded by the formation of an oxime (VIIIa, 87%) or a semicarbazone (VIIId, 76%). The proton magnetic resonance spectra of the oximes (VIa–c) made it quite clear that the ring had opened in the indicated manner. On

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(1) For the preceding communication of this series, see C. K. Bradsher and J. D. Turner, *J. Org. Chem.*, **31**, 565 (1966).

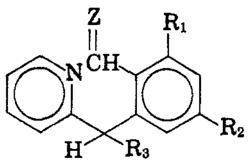
(2) This investigation was supported by Public Health Service Research Grant No. CA-05509 of the National Cancer Institute.

(3) W. Schneider and K. Schroeter, *Ber.*, **53**, 1459 (1920).

(4) J. G. Frost and J. H. Saylor, *Rec. Trav. Chim.*, **82**, 828 (1963).

(5) A. Richards and T. S. Stevens, *J. Chem. Soc.*, 3067 (1958).

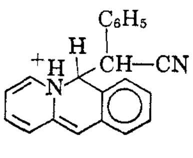
(6) C. K. Bradsher and J. H. Jones, *J. Am. Chem. Soc.*, **81**, 1938 (1959).



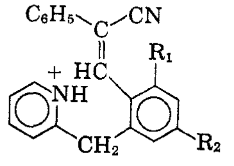
VIa, $R_1 = R_2 = R_3 = H$; $Z = NOH$
b, $R_1 = CH_3$; $R_2 = R_3 = H$; $Z = NOH$
c, $R_1 = H$; $R_2 = Cl$; $R_3 = CH_3$; $Z = NOH$
d, $R_1 = R_2 = R_3 = H$; $Z = NNHCONH_2$

refluxing for 1 hr in 48% hydrobromic acid, the unsubstituted oxime (VIa) was converted to acridizinium bromide in 91% yield.

Reexamination by use of nmr of the products obtained by hydroxide ion catalyzed condensation of phenylacetonitrile with the acridizinium ion has shown unequivocally that the product has structure VIIIa, rather than VII as suggested previously.[6] This result is explicable if one assumes that the formylbenzylpyridine (V) is an intermediate in the condensation reaction.

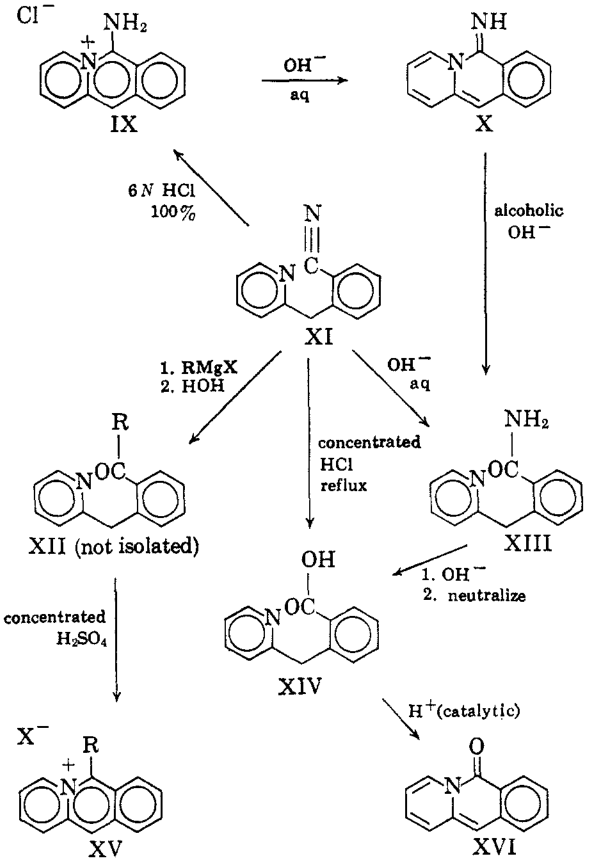


VII

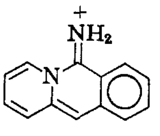


VIIIa, $R_1 = R_2 = H$
b, $R_1 = CH_3$; $R_2 = H$
c, $R_1 = H$; $R_2 = CH_3$

SCHEME I



Since aziridizinium bromide can be prepared in 82% yield from benzyl bromide and picolinaldoxime and converted to 2-(2-oximidomethylbenzyl)pyridine (VIIIa) in 87% yield, the latter is conveniently available in an over-all yield of 71%. It appeared of particular interest to see whether the oxime (VIIIa) might be converted to the corresponding nitrile (XI), a potential intermediate in other cyclization reactions. The usual acidic reagents for conversion of oximes to nitriles converted oximidomethylbenzylpyridine (VIIIa) to intractable materials, but success was achieved (78% yield of XI) by treating the sodium salt of the oxime with *p*-toluenesulfonyl chloride. The new nitrile (XI) served as the starting point for some interesting transformations (Scheme I). Heating the nitrile (XI) at 100° in 6 *N* hydrochloric acid afforded a yellow salt which in trifluoroacetic acid showed a proton magnetic resonance spectrum devoid of a signal for the methylene group which was present in the starting material. The ultraviolet absorption spectrum suggests that the salt is the previously unknown 6-aminoacridizinium chloride (IX). Treatment of an aqueous solution of the yellow salt with sodium hydroxide solution afforded an orange precipitate soluble in organic solvents. The ultraviolet absorption spectrum of the new base was very similar to that of 6-aminoacridizinium chloride and the proton magnetic resonance spectrum revealed no aliphatic-type protons. Analytical as well as spectral evidence suggested that the new base was 6H-benzo[*b*]quinolizin-6-one imine (X) produced by the loss of a proton from the amino group of 6-aminoacridizinium cation (IX). The acidic nature of the protons of the amino group can best be understood by examining another canonical form (IXb) contributing to the resonance hybrid designated as IX.



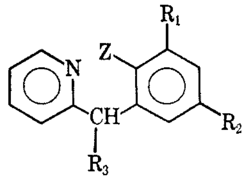
IXb

When imine X was refluxed with alcoholic potassium hydroxide, the colorless 2-(2-carboxamidobenzyl)pyridine (XIII) was formed. The pmr spectrum had a singlet at 4.66 ppm (two protons) owing to the methylene group, and the infrared spectrum showed an amide carbonyl group at 6.0 μ. The same amide (XIII) was obtained by incomplete alkaline hydrolysis of the nitrile (XI).

When the amide (XIII) was subjected to more drastic alkaline hydrolysis, and the pH of the solution was properly adjusted, the amphoteric 2-(2-carboxybenzyl)pyridine (XIV) was obtained. The acid, which showed an infrared absorption band at 5.85 μ, could not be purified by recrystallization and was obtained in a state of analytical purity by precipitation from either acidic or basic solution. The most convenient method for obtaining the acid (XIV) was by hydrolysis of the nitrile (XI) in boiling hydrochloric acid. The acid (XIV), on refluxing in water containing a trace of mineral acid, cyclized to afford a yellow insoluble compound which showed an absorption at 5.98 μ in the infrared spectrum (amide carbonyl), and was insoluble in dilute acid or base. On the basis of its composition, melting point, and ultraviolet absorption spec-

TABLE I

NUCLEAR MAGNETIC RESONANCE DATA FOR 2-BENZYLPYRIDINE DERIVATIVES



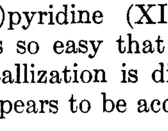
Substituents				Protons on bridge carbon			Nonaromatic protons elsewhere		
R_1	R_2	R_3	Z	No.	Pattern	δ, ppm	No.	Pattern	δ, ppm
...	...	...	...	2	Singlet	4.46	...	...	...
...	...	...	CH=C(CN)Ph	2	Singlet	4.73	...[a]	...	...
Me	...	...	CH=C(CN)Ph	2	Singlet	4.68	3[a]	Singlet	2.34
...	Me	...	CH=C(CN)Ph	2	Singlet	4.72	3[a]	Singlet	2.73
...	...	...	CH=NOH	2	Singlet	4.60	...	...	...
Me	...	...	CH=NOH	2	Singlet	4.96	3[b]	Singlet	2.92
...	Cl	CH_3	CH=NOH	1	Quartet	5.14	3[b]	Doublet	1.92
...	...	...	CN	2	Singlet	4.60	...	...	...
...	...	...	CH_2OH[c]	2	Singlet	4.72	2[d]	Singlet	5.60
...	...	...	$CONH_2$	2	Singlet	4.66	...[e]	...	...

[a] The styryl proton of the side chain gives a signal which was not distinguishable from those of the aromatic protons. [b] For methyl group. [c] As methoperchlorate. [d] Assigned to methylene protons of carbinol group. The protons of the N-methyl group appeared as a singlet at 4.48 ppm. [e] The protons attached to nitrogen were not identified.

trum, the cyclization product is believed to be 6H-benzo[*b*]quinolizin-6-one (XVI), previously obtained in 9% yield by Paquette[7] by oxidation of the acridizinium cation with alkaline ferricyanide. The conversion of 2-(carboxybenzyl)pyridine (XIV) to the benzoquinolizone (XVI) is so easy that purification of the acid (XIV) by crystallization is difficult and melting of the acid (XIV) appears to be accompanied by cyclization.

It was anticipated that benzoquinolizin-6-one (XVI) in concentrated sulfuric acid might undergo protonation to afford the 6-hydroxyacridizinium ion, but the ultraviolet absorption spectrum gave no evidence for such a change (one maximum, at 281 mμ).

A crude methyl ketone (XII, R = CH_3), obtained from the nitrile *via* the addition of methylmagnesium iodide, was cyclized in concentrated sulfuric acid to yield the 6-methylacridizinium cation (XV, R = CH_3) which (as the bromide) was identical with that reported earlier.[8] In an analogous fashion 6-phenylacridizinium ion (XV, R = C_6H_5) was obtained, and the ultraviolet absorption spectrum of the new cation (as the perchlorate) was found to be very similar to that of the isomeric 11-phenylacridizinium cation.[9] An earlier claim[6] to have prepared the picrate of 6-phenylacridizinium ion by dehydrogenation of the base (formulated as XVII) obtained by reaction of



XVII

acridizinium bromide with phenylmagnesium bromide is erroneous. It has been shown that the supposed dehydrogenation product which was obtained earlier by boiling the base in ethanolic picric acid is simply the picrate of the base.

Since the research described in this paper has been so much concerned with derivatives of 2-benzylpyridine it was felt important to summarize in Table I the nmr data obtained for such compounds.

Experimental Section

All analyses were made by Ilse Beetz Mikroanalytisches Laboratorium, Kronach, Germany, or Dr. C. Janssen Research Laboratorium, Beerse, Belgium. Melting points were determined in capillaries using a Laboratory Devices Mel-Temp block and are uncorrected. Ultraviolet absorption spectra were measured in 95% ethanol using 1-cm quartz cells with a Cary Model 14 spectrophotometer. The solvents used in nmr determinations were deuteriochloroform for the bases and trifluoroacetic acid for the salts. All infrared spectra were determined in potassium bromide plates.

Precipitation of Base from Acridizinium Bromide Solution.—To a rapidly stirred solution of 1 g of acridizinium (III) bromide[10] in water, 10% sodium hydroxide solution was added dropwise until precipitation was complete. The precipitate was collected, washed with water until the filtrate was free of inorganic ions, and air dried on the filter for 2 hr, yielding 0.58 g (75%) of an orange powder. The infrared spectrum showed a weak absorption at 5.9 μ (carbonyl). The analytical sample was obtained as an orange microcrystalline powder (mp 75–77°), by drying the precipitate under reduced pressure at 56° for 24 hr, and from the nmr and ultraviolet data appeared to be a mixture: nmr (deuteriochloroform), δ 4.60 and 5.10 [methylene protons of the aldehyde (V) and the proton of C-6 of the psuedo base (IV)], signals centered at 6.60 and 10.86 (attributed to hydroxyl proton of pseudo-base, and the aldehydic proton of the aldehyde, respectively); the ultraviolet spectrum (in 95% ethanol) showed the usual acridizinium absorption peaks[10a] plus an additional peak at 417 mμ, attributed to the pseudo-base. The ethanol solution of the base showed the characteristic acridizinium fluorescence.

Anal. Calcd for $C_{13}H_{11}NO \cdot 0.25\ H_2O$: C, 77.39; H, 5.74; N, 6.94. Found: C, 77.51; H, 5.65; N, 7.00.

General Procedure for the Preparation of 2-(2-[α-cyanostyryl]-benzyl)pyridines (VIII).—The appropriate[10a] acridizinium bromide (0.00364 mole) was refluxed for 5 hr in 30 ml of ethanol containing 1 g of phenaylacetonitrile and 0.6 g of potassium hydroxide. The ethanol was removed *in vacuo*, water was added, and the mixture was extracted with ether. After the ethereal extract had been dried, hydrogen bromide was passed in. After the

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(7) L. A. Paquette, *Chem. Ind.* (London), **28**, 1292 (1962).

(8) C. K. Bradsher and J. C. Parham, *J. Heterocyclic Chem.*, **1**, 121 (1964).

(9) C. K. Bradsher and T. W. G. Solomons, *J. Am. Chem. Soc.*, **81**, 2550 (1959).

(10) (a) C. K. Bradsher and L. E. Beavers, *ibid.*, **77**, 4812 (1955); (b) C. K. Bradsher, T. W. G. Solomons, and F. R. Vaughn, *J. Org. Chem.*, **25**, 757 (1960).

mixture had stood in the refrigerator overnight, the solid precipitate was collected and recrystallized from methanol–ethyl acetate.

2-(2-[α-Cyanostyryl]benzyl)pyridine Picrate.—The light yellow, irregular crystals of the hydrobromide of VIIIa could not be recrystallized and were used without purification for the nmr observations. Addition of picric acid solution to a solution of the crude hydrobromide afforded the known picrate (yellow needles, mp 149–151°) from ethanol (lit.[6] mp 151–151°) and was shown to be identical by comparison of infrared spectra.

2-(2-[α-Cyanostyryl]-3-methylbenzyl)pyridine Hydrobromide (VIIIb).—The product was obtained in 67% yield as colorless, irregular crystals, mp 198–199°.

Anal. Calcd for $C_{22}H_{19}BrN_2 \cdot 0.25H_2O$: C, 66.75; H, 4.96; N, 7.08. Found: C, 66.44; H, 4.96; N, 7.11.

A **picrate** (mp 174–176°) was prepared from the bromide and found to be identical with that previously reported (lit.[6] mp 176–178°).

2-(2-[α-Cyanostyryl]-5-methylbenzyl)pyridine Hydrobromide (VIIIc).—The product was obtained in 49% yield as colorless needles, mp 195–197° with gas evolution.

Anal. Calcd for $C_{22}H_{19}BrN_2$: C, 67.52; H, 4.89; N, 7.16. Found: C, 67.46; H, 4.86; N, 7.18.

The **picrate** (mp 180–182°) was identical with that previously reported (lit.[6] mp 183–184°).

1-Methyl-2-(2-hydroxymethyl)pyridinium Perchlorate.—A solution containing 1.3 g of acridizinium bromide and 1 g of potassium hydroxide was stirred and 0.5 g of sodium borohydride was added. The solution was poured into water and the product was recovered by extraction with ether. The ethereal solution was dried and concentrated leaving a red oil which was refluxed overnight in a mixture containing 10 ml each of reagent grade acetone and methyl iodide. The solution was concentrated yielding what was presumably the methiodide (VIIIe), mp 196–197°, 0.99 g (58%). This material was dissolved in hot water and treated with a solution of sodium perchlorate. The analytical sample of the perchlorate (VIIIf) crystallized from methanol–ethyl acetate as colorless plates, mp 138–140°.

Anal. Calcd for $C_{14}H_{16}ClNO_5$: C, 53.59; H, 5.14; N, 4.47. Found: C, 53.38; H, 5.07; N, 4.51.

2-(2-Oximidomethylbenzyl)pyridine (VIa). A. From Pure Acridizinium Bromide.—A solution of 0.36 g of hydroxylamine hydrochloride, neutralized by addition of excess sodium bicarbonate, was rapidly added to a stirred solution containing 1 g of acridizinium bromide in 15 ml of water. A tan powder precipitated immediately, but stirring was continued for 30 min. The mixture was cooled and the product was collected and recrystallized from ethanol–water yielding 0.71 g (87%) of elongated colorless plates, mp 156–157°.

B. From 1-Benzyl-2-(oximidomethyl)pyridinium Bromide (Preparative Method).—Acridizinium bromide is formed in excellent yield by the cyclization of 1-benzyl-2-(oximidomethyl)-pyridinium bromide,[10b] but the product is contaminated with hydroxylamine hydrobromide which, owing to double salt formation, is difficult to remove without loss of product. Since hydroxylamine is needed in the ring-opening reaction, a convenient route to oximidomethylbenzylpyridine (VIa) avoids the isolation of pure acridizinium bromide. Ten grams of 1-benzyl-2-(oximidomethyl)pyridinium bromide[10b] was refluxed for 0.5 hr in 50 ml of 48% hydrobromic acid, and the acid was removed *in vacuo* (aspirator). Water was added to dissolve the residue and was removed *in vacuo*. After the addition and removal of water had been repeated, the residue was dissolved in 250 ml of water, and the solution was neutralized by addition of sodium bicarbonate. To this solution, a neutralized solution of 10 g of hydroxylamine hydrochloride was added rapidly. The mixture was adjusted to a pH of about 8 by the addition of sodium bicarbonate and stirred for 0.5 hr. The product (6.0 g, 83% yield) was collected and recrystallized from dilute ethanol. This represents an over-all yield of 72% from picolinaldoxime.

Anal. Calcd for $C_{13}H_{12}N_2O$: C, 73.56; H, 5.70; N, 13.20. Found: C, 73.68; H, 5.77; N, 13.34.

The **methiodide** was obtained by refluxing VIa for 6 hr with methyl iodide in methanol and acetone. The analytical sample crystallized from methanol–ethyl acetate as colorless prisms, mp 178–180°.

Anal. Calcd for $C_{14}H_{15}IN_2O$: C, 47.47; H, 4.27; N, 7.91. Found: C, 47.80; H, 4.31; N, 7.88.

The **methoperchlorate**, prepared from the methiodide, crystallized from methanol–ethyl acetate as colorless plates, mp 159–161°.

Anal. Calcd for $C_{14}H_{15}ClN_2O_5$: C, 51.46; H, 4.63; N, 8.58. Found: C, 51.42; H, 4.72; N, 8.85.

Cyclization of 2-(2-Oximidomethylbenzyl)pyridine (VIa).—A solution of 2 g of 2-(2-oximidomethylbenzyl)pyridine (VIa) in 20 ml of 48% hydrobromic acid was refluxed for 1 hr. The reaction mixture was diluted to 120 ml and cooled while a solution containing molecularly equivalent quantities of bromine and hydrobromic acid was added dropwise. When precipitation was complete, the solution was cooled and the precipitate was collected and washed with cold water. The resulting tribromide salt was dissolved in 100 ml of a mixture of acetone and methanol. The solution was concentrated and ethyl acetate was added. The cooled solution yielded 2.23 g (91%) of acridizinium (III) bromide, mp 240–243°, which was identical with an authentic sample.

2-(2-Oximidomethyl-3-methylbenzyl)pyridine (VIb).—The title compound was prepared essentially as in the case of the lower homolog and crystallized from ethanol–water as colorless crystals, mp 129–131°.

Anal. Calcd for $C_{14}H_{14}N_2O$: C, 74.31; H, 6.24; N, 12.38. Found: C, 74.13; H, 6.26; N, 12.39.

2-(α-Methyl-2-oximidomethyl-5-chlorobenzyl)pyridine (VIc) was prepared essentially in the same way as the parent compound (VIIIa). The analytical sample crystallized from ethanol–water as irregular tan prisms, mp 148–149.5°.

Anal. Calcd for $C_{14}H_{13}ClN_2O$: C, 64.49; H, 5.02; N, 10.75. Found: C, 64.59; H, 5.01; N, 10.75.

2-(2-Formylbenzyl)pyridine Semicarbazone (VId).—This preparation was carried out (76% yield) essentially as the preparation of VIa from acridizinium bromide except that a neutralized solution of semicarbazide hydrochloride was added instead of hydroxylamine. The analytical sample crystallized from ethanol–water as long, colorless needles, mp 171–173°.

Anal. Calcd for $C_{14}H_{14}N_4O$: C, 66.12; H, 5.55; N, 22.03. Found: C, 65.95; H, 5.66; N, 22.01.

2-(2-Cyanobenzyl)pyridine (XI).—To a stirred solution of 30 g of 2-(2-oximidomethylbenzyl)pyridine (VIIIa) in 225 ml of 10% sodium hydroxide solution, 30 g of *p*-toluenesulfonyl chloride was added in small portions over a 15-min period. After 1 hr, the oil was extracted from the cooled solution with ether and the ethereal extracts were washed and dried. The ethereal solution was concentrated and the residue was twice distilled under reduced pressure yielding 21.55 g (78%) of a viscous, yellow liquid, bp 127–130° (0.8 mm). The analytical sample boiled at 129° (0.8 mm) and the spectrum showed a strong infrared absorption at 4.43 mμ (nitrile).

Anal. Calcd for $C_{13}H_{10}N_2$: C, 80.38; H, 5.19; N, 14.43. Found: C, 80.08; H, 5.25; N, 14.75.

The **picrate** was prepared in ethanolic solution and formed small yellow needles, mp 215–216°.

Anal. Calcd for $C_{19}H_{13}N_5O_7$: C, 53.90; H, 3.09; N, 16.55. Found: C, 53.58; H, 3.29; N, 16.71.

6-Aminoacridizinium Chloride (IX).—A solution of 1 g of 2-(2-cyanobenzyl)pyridine (XI) in 25 ml of 6 *N* hydrochloric acid was heated on a steam bath for 2 hr. The yellow needles which precipitated during the reaction were collected and washed with ether yielding 0.84 g (69%). The analytical sample crystallized from dilute hydrochloric acid as small yellow needles, mp 281° with previous sublimination beginning at 265°.

Anal. Calcd for $C_{13}H_{11}ClN_2 \cdot 0.25H_2O$: C, 66.38; H, 4.93; N, 11.91. Found: C, 66.27; H, 4.99; N, 11.88.

The analytical sample of the **perchlorate** crystallized from dilute acetic acid as small yellow needles: mp 254–256°; λ_{max} 235 mμ sh (log ε 4.55), 241 (4.56), 257 sh (4.25), 340 sh (3.68), 380 (4.06), 405 (4.04), 427 (3.88).

Anal. Calcd for $C_{13}H_{11}ClN_2O_4$: C, 52.98; H, 3.76; N, 9.51. Found: C, 52.95; H, 3.78; N, 9.43.

The **picrate** was prepared from the chloride in ethanolic solution. The analytical sample crystallized from ethanol as yellow needles, mp 213.5–214.5°.

Anal. Calcd for $C_{19}H_{13}N_5O_7$: C, 53.90; H, 3.09; N, 16.54. Found: C, 53.76; H, 3.07; N, 16.42.

6H-Benzo[b]quinolizin-6-one Imine (X).—To a stirred solution of 0.08 g of 6-aminoacridizinium chloride (IX) in 100 ml of water, 10% sodium hydroxide solution was added until precipitation was complete. The orange powder was collected and washed with water. This powder crystallized from ligroin (bp 60–90°)

as orange needles: mp 109–111°; yield 0.57 g (80%); λ_{max} 230 mμ (log ϵ 4.50), 235 sh (4.48), 241 sh (4.45), 260 sh (4.12), 325 sh (3.49), 337 (3.58), 387 sh (3.98), 403 (4.01), 429 sh (3.84), 450 sh (3.66), 475 sh (3.30).

Anal. Calcd for $C_{13}H_{10}N_2$: C, 80.38; H, 5.19; N, 14.43. Found: C, 79.92; H, 5.21; N, 14.58.

2-(2-Carboxamidobenzyl)pyridine (XIII). A. From 6H-Benzo[*b*]quinolizin-6-one Imine (X).—A solution containing 0.55 g of benzo[*b*]quinolizin-6-one imine (X) and 2 g of potassium hydroxide in 50 ml of ethanol was refluxed for 12 hr during which time the orange solution became colorless. The alcohol was evaporated and the product was precipitated by addition of water. The precipitate crystallized from ethanol–water yielding 0.48 g (80%) of colorless product, mp 191–196°. The infrared spectrum of the product showed a strong absorption at 6.00 μ (primary amide carbonyl). The analytical sample consisted of colorless plates, mp 197–199°.

B. From 2-(2-Cyanobenzyl)pyridine (XI).—To a solution containing 25 ml of 25% potassium hydroxide and 5 ml of ethanol, 1 g of 2-(2-cyanobenzyl)pyridine (XI) was added and the mixture was refluxed for 24 hr. On cooling the colorless solution yielded 0.42 g (39%) of colorless plates, mp 197–199°, identical (infrared spectrum) with the product obtained by procedure A. Since ammonia was detected during the reaction, it seems probable that a better yield might be obtained under less drastic conditions.

Anal. Calcd for $C_{13}H_{12}N_2O$: C, 73.56; H, 5.70; N, 13.20. Found: C, 73.43; H, 5.68; N, 13.35.

2-(2-Carboxybenzl)pyridine (XIV). A. From 2-(2-Cyanobenzyl)pyridine (XI).—A solution of 1 g of the nitrile (XI) in 20 ml of concentrated hydrochloric acid was refluxed for 24 hr, the acid was removed under vacuum, and the residue was dissolved in 50 ml of water. Aqueous ammonia was added until the pH reached 7, precipitating a colorless powder, 0.80 g (73%), mp 139–140°. The analytical sample was prepared by reprecipitation of the powder from dilute hydrochloric acid followed by drying at room temperature, mp 140–141°.

B. From 2-(2-Carboxamidobenzyl)pyridine (XIII).—To a mixture of 45 ml of 10% sodium hydroxide solution and 5 ml of ethanol, 1.06 g of the amide (XIII) was added and the mixture was refluxed for 24 hr. The solution was cooled, filtered, and adjusted to pH 7. The resulting powder was reprecipitated from dilute hydrochloric acid, yielding 0.5 g (41%) of a colorless microcrystalline powder, mp 140–141°, identical with the material obtained by procedure A.

Anal. Calcd for $C_{13}H_{11}NO_2$: C, 73.22; H, 5.20; N, 6.57. Found: C, 72.83; H, 5.13; N, 6.76.

6H-Benzo[*b*]quinolizin-6-one (XVI).—A solution of 100 mg of 2-(2-carboxybenzyl)pyridine (XIV) in 20 ml of water containing 1 drop of 6 *N* hydrochloric acid was refluxed for 12 hr. The precipitate crystallized from ethanol as 70 mg (76%) of yellow needles, mp 164–165°. The infrared spectrum showed a strong peak at 5.98 μ (amide carbonyl). The analytical sample melted at 164–165° (lit.[7] mp 162–164°).

Anal. Calcd for $C_{13}H_9NO$: C, 79.98; H, 4.65; N, 7.18. Found: C, 79.78; H, 4.48; N, 7.30.

6-Methylacridizinium Perchlorate (XV, $R = CH_3$; $X = ClO_4$).—Methylmagnesium iodide was prepared from 3.65 g of methyl iodide and the ether was replaced with anhydrous benzene. To the refluxing benzene solution, a solution of 2 g of 2-(2-cyanobenzyl)pyridine in 25 ml benzene was added. Refluxing was continued for 10 hr, then the benzene was displaced by addition of 6 *N* hydrochloric acid. The aqueous solution was heated at 100° for 2 hr, then worked up in the usual way affording about 2 ml of a dark oil which exhibited a peak at 5.9 μ (ketone carbonyl).

The crude ol was dissolved in 10 ml of concentrated sulfuric acid by warming for a few minutes on the steam bath. The acid solution was allowed to stand at room temperature for 5 hr, then poured into 200 ml of anhydrous ether. The resulting mixture was allowed to stand in the refrigerator overnight and the ether was decanted from the precipitated oil. The oil was dissolved in 25 ml of water, the solution was charcoaled, and 35% perchloric acid was added. The precipitate was collected and crystallized from water, yielding 0.33 g (11%) of yellow needles, mp 212–213° (lit.[9] mp 213–214°).

The **picrate**, mp 173–174°, crystallized from ethanol–ethyl acetate as a yellow, microcrystalline powder and was identical in all respects with an authentic sample (lit.[9] mp 174–175°).

6-Phenylacridizinium Perchlorate (XV, $R = C_6H_5$; $X = ClO_4$).—If in the procedure used in the preparation of 6-methylacridizinium (XV, $R = CH_3$) the methylmagnesium iodide was replaced by phenylmagnesium bromide from 4.05 g of bromobenzene, the product was 0.3 g (8%) of yellow needles. The analytical sample crystallized from methanol–ethyl acetate as yellow needles: mp 249–250° dec; λ_{max} 248 mμ (log ϵ 4.63), 285 sh (4.00), 345 sh (3.70), 363 (3.93), 386 (3.96), 406 (3.93).

Anal. Calcd for $C_{19}H_{14}ClNO_4$: C, 64.14; H, 3.97; N, 3.94. Found: C, 64.15; H, 4.00; N, 3.93.

The Nature of the 6-Phenylacridizinium Picrate of Bradsher and Jones [6]—The 6-phenylacridizinium perchlorate could be converted to a picrate, mp 185–186°, which was not identical with the picrate, mp 188–190.5°, described earlier[6] as the dehydrogenation product of the base XVII. Since a sample of the base was still available, we were able to establish that the supposed dehydrogenation product was simply the picrate of base XVII and that no dehydrogenation occurred during refluxing of the base with picric acid.

Registry No.—2-Benzylpyridine, 101-82-6; VIIIa, 7547-77-5; VIIIb, 7547-78-6; VIIIc, 7561-81-1; VIa, 7561-82-2; VIb, 7547-79-7; VIc, 7547-80-0; XI, 7547-81-1; VIIIf, 7547-82-2; XIII, 7547-83-3; III OH; 7547-84-4; VIIIa picrate, 7603-38-5; VIIIb hydrobro, mide, 7547-85-5; VIIIc hydrobromide, 7547-86-6-VIIIe, 7551-31-7; VIa methiodide, 7551-32-8; VIa methoperchlorate, 7547-87-7; III bromide, 7547-88-8; VId, 7551-33-9; XI picrate, 7547-89-9; IX chloride, 7547-90-2; IX perchlorate, 7547-91-3; IX picrate, 7650-62-6; X, 7561-83-3; XIV, 7561-84-4; XVI, 7547-92-4; XV ($R = Me$; $X = ClO_4^-$), 7547-93-5; XV ($R = C_6H_5$; $X = ClO_4$), 7547-94-6.