oxidative work-up of the ozonolysis mixture with alkaline peroxide has produced **4**,[6d] while permanganate in aqueous pyridine oxidative decomposition has led to benzo[*d*]diphenic acid.[9a] The two methyl substituents in **1**, however theoretically, should introduce two competitive effects not present in benz[*a*]anthracene.

(i) Hyperconjugation with the aromatic moiety in **1** should enhance the electron density and, consequently, ozone attack at both the L-region, and to a lesser extent, the K-region.

(ii) Increased steric hindrance to ozone attack at the L-region should lower reaction at these sites.

On the basis of only 45% of the starting material accounted for in the 1:1 mole ratio runs, and 63% in the 2.5:1 mole ratio runs, both effects seem operative (L-region attack by ozone *is decreased* in the strongly carcinogenic **1**, relative to benz[*a*]anthracene, while simultaneous K-region cleavage *is increased*). No clean separation of these competitive factors could be derived however from the present study. Also unknown is the site of attack on that portion of **1** which is unaccounted for. The observed mode of attack on **1** by ozone, however, would be expected from Pullmans' K-region theory of carcinogenesis.

The mechanism of electrophilic ozone attack of aromatic bonds, to yield cleavage products **4**, **5**, **6**, and **7**, and reactive sites, to give **3**, has been thoroughly discussed elsewhere.[6d,e,7b,d,15,16]

Tetracyclic Phenothiazines. V. Brominations and Dehydrobrominations of Some Pyrido[3,2,1-*kl*]phenothiazines[1]

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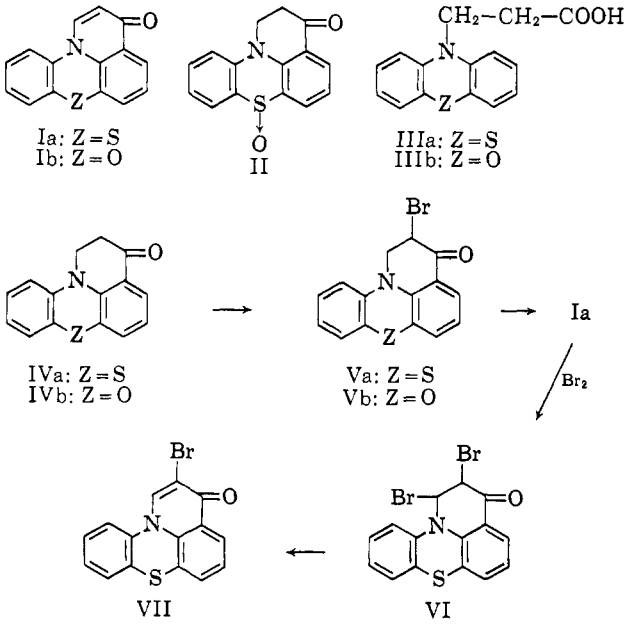
Bromination of 2,3-dihydro-3-keto-1*H*-pyrido[3,2,1-*kl*]phenothiazine (IVa) gave the 2-bromo derivative. This dehydrohalogenated essentially quantitatively on attempted reaction with a variety of nucleophiles. The resulting 3-keto-1*H*-pyrido[3,2,1-*kl*]phenothiazine (Ia), which has been considered "aromatic" in some respects, *adds* bromine to its dihydropyridone double bond to give VI. Compound VI dehydrohalogenates readily, *e.g.*, on solution in polar solvents. An improved synthesis of IVa is given.

A recent publication has mentioned the accidental preparation[2] and one, still more recently, the deliberate synthesis[3] of the phenothiazine Ia. The unplanned synthesis of what was presumed to be the analogous phenoxazine derivative Ib has also been reported recently.[4]

The phenothiazine, Ia, was first made by treatment of the sulfoxide, II, with hot aqueous ethanolic hydrochloric acid in an unsuccessful attempt to make a derivative of Ia chlorinated on one or both of the benzene rings. The rational preparation of Ia was by palladium-catalyzed dehydrogenation of IVa. What is probably the phenoxazine analog Ib was formed, together with the anticipated ketone IVb, by the cyclization of the phenoxazine N-propionic acid IIIb under relatively mild conditions.

Discussion of the high melting point and of the ultraviolet and infrared absorption of Ia have been given in terms of the "aromatic nature" of this substance, a point exhaustively debated in the past in connection with both 2- and 4-pyridones. However, little is known about the reactions of 2,3-dihydro-4-(1*H*)-quinolones, of which the compounds IV and V are examples[5] nor about 4-(1*H*)-quinolones such as the compound I.

We have found in the course of work directed at the preparation of amine-substituted derivatives of this ring system, that the compound Ia, whether "aromatic" or not, is the only product obtained in appreciable



amount upon treatment of the monobromo ketone Va with a variety of nucleophilic reagents. These have included sodium thiophenolate (a reagent known generally to give rapid SN2 reactions), dimethylamine (neat, in ether, in isopropyl alcohol, or in other solvents of varying polarities), anhydrous ammonia in absolute ethanol, and sodium acetate in acetic acid (a reagent which frequently gives a ratio of substitution to elimination higher than that of some other nucleophilic reagents, presumably because it leads to a reaction more nearly approximating the SN1 type). Indeed, merely keeping Va in dimethyl sulfoxide solution at room temperature for eighteen hours and subsequent dilution with water or a moderately prolonged attempt to

(1) Previous paper, M. Harfenist, *J. Org. Chem.*, **28**, 538 (1963).

(2) O. Hromatka, M. Knollmüller, and F. Sauter, *Monatsh. Chem.*, **93** 723 (1962).

(3) J. A. VanAllan, G. A. Reynolds, and R. E. Adel, *J. Org. Chem.*, **27**, 1659 (1962).

(4) P. Müller, N. P. Buu-Hoi, and R. Rips, *ibid.*, **24**, 1699 (1959).

(5) The work of F. G. Mann and his associates, some of which is discussed in connection with our results, is a notable exception. For a leading reference, see P. I. Ittyerah and F. G. Mann, *J. Chem. Soc.*, 467 (1958).

recrystallize Va from boiling methanol–water led to isolation of Ia in good yield.

One diagnostic criterion (of many) advanced to define aromaticity[6] is the substitution of a hydrogen attached to an aromatic system by reagents which, in contrast, react with "ordinary" double bonds by addition. It is, therefore, of interest that Ia, on reaction with bromine in carbon tetrachloride, *adds* bromine to give VI. The crude product of bromination, produced in essentially quantitative yield, was an orange solid which had a fairly wide melting point range. Elemental analysis of this crude material gave a bromine analysis about 1% too high, and a carbon analysis several per cent under the theoretical. This probably is due to contamination of VI by a small amount of the tribromo compound produced from VI by dehydrohalogenation and addition of bromine to the resulting VII. Acceptable analyses of VI were obtained, however, after it was purified.[7]

It would be expected that VI would have its bromines *trans*, and hence that dehydrohalogenation, which should require a hydrogen *trans* to a bromine, might not occur readily. However, it is known that α,β-dibromocyclohexanones often dehydrohalogenate easily.[8] In the case of compound VI it was found that reaction with dimethylamine in toluene, recrystallization from hot nitromethane, or attempted recrystallization from ethanol–water led entirely to dehydrohalogenation to a neutral bromine-containing product, presumably VII.

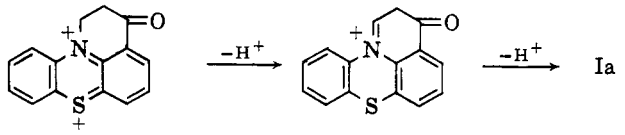
Finally, while VII added bromine in carbon tetrachloride solution with a concomitant change in the appearance of the solution and precipitation of a solid, the product proved difficult to purify sufficiently for adequate characterization. It may well consist of some S-bromo compound and/or the product of addition to the double bond. This product or products reverted to VII on recrystallization from ethanol–water at the boiling point. While this behavior is what one would expect from a substance in the oxidation state of an S-bromo compound, we cannot rule out the possibility of the compound being that produced by addition of bromine to the double bond of VII. For example the dibromo amide VIII has recently been reported[9] to revert to the N,N-diethylcinnamamide from which it was made upon treatment with a representative assortment of nucleophiles.

$C_6H_5CHBrCHBrCON(C_2H_5)_2$
VIII (*erythro*)

Discussion

The compounds IV correspond to structures that would be listed as 1-aryl-1,2,3,4-tetrahydro-4-oxoquinolines, or 1-aryl-2,3-dihydro-4-(1*H*)-quinolones in *Chemical Abstracts*. Although related structural features are found in many natural products, few examples are reported in the literature which are analogous to our experimental results. The simplest analogous compounds, the 1-phenyl- and 1-methyl-4-oxo-1,2,3,4-tetrahydroquinolines, are reported[5] to give a mixture of bromo compounds on direct bromination, from which no 3-bromo compound was obtained. Similarly, use of N-bromosuccinimide was reported to give a mixture of 6-bromo and 6,7-dibromo derivatives of the 4-oxotetrahydroquinoline. It is rather surprising that bromination of the benzene ring, which is deactivated for electrophilic reactions by the carbonyl group, should have occurred in these simple tetrahydro-4-oxoquinolines, rather than bromination α to the carbonyl group, while bromination of our dihydropyridophenothiazine IVa, which contains a benzene ring activated by an arylamino group and feebly activated or feebly deactivated by the arylthio group, nonetheless occurs α to the carbonyl group.[10]

It is recognized that the monobromination product of IVa which we have formulated as Va could be an S-bromo compound. This then might dehydrohalogenate to Ia by way of an intermediate IX as we believe occurs in Hromatka's preparation of Ia from the sulfoxide II. This proposal is an extension of the mechanism suggested[11] for the preparation of 3-chlorophenothiazine and 3,7-dichlorophenothiazine from phenothiazine 5-oxide. We have formulated our monobromo compound as Va rather than as an S-bromo compound, on the grounds of its stability in refluxing ethyl acetate, since other related S-bromo compounds are reported to be decomposed by temperatures above room temperature, and because no evidence of attack of various nucleophiles on the benzene ring was observed (compare ref. 11).



IX

However, dehydrohalogenation reactions similar in many respects to those reported here were found[12] to occur upon treatment of the bromothiochromanone X with a variety of nucleophiles, generally in water or in 95% ethanol solution. It is apparent that the alicyclic ring and one benzene ring are analogous in Xa and Va, but that Xa has a sulfur where Va has a nitrogen. Two reactions are reported to occur with Xa, however, which we have not observed with Va, although their occurrence to a slight degree cannot be completely excluded. Treatment of Xa with dry ammonia in absolute ethanol is reported to give the 3-amino compound, which forms a hydrochloride.

As was mentioned, treatment of Va with the same reagent leads to dehydrohalogenation. No acid-soluble product was found, when the attempted amina-

(6) For a more sophisticated discussion, see for example, A. T. Balaban and Z. Simon, *Tetrahedron*, **18**, 315 (1962).

(7) Crude VI could be recrystallized from much ethyl acetate to a reasonably constant melting point about 153°. Twice, a considerably higher melting point (about 184°) was obtained, presumably due to thermal dehydrohalogenation of VI in the Pyrex capillary melting point tube without macroscopically detectable melting of the solid. Indeed a 24-hr. heating of the solid at 78°, in an attempt to dry an analytical sample, led to extensive loss of bromine. However, it was possible to dry a sample satisfactorily at this temperature for a shorter period.

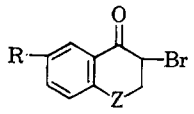
(8) F. G. Bordwell and R. J. Kern, *J. Am. Chem. Soc.*, **77**, 1141 (1955), give examples of other dehydrohalogenations in which a more acidic initially *cis* hydrogen is lost in preference to a less acidic *trans* hydrogen.

(9) A. J. Speziale and C. C. Tung, Abstracts of Papers, 93Q, Division of Organic Chemistry, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1962.

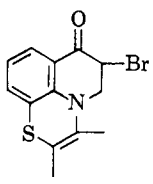
(10) Indeed, it is rather surprising that 1-phenyl-4-oxo-1,2,3,4-tetrahydroquinoline is reported to brominate in the 6-position of the quinoline benzene ring, rather than in the benzene ring attached to N1, which would be activated by the alkylamino group and not deactivated by the carbonyl group, if ionic bromination were being observed.

(11) A. C. Schmalz and A. Burger, *J. Am. Chem. Soc.*, **76**, 5455 (1954).

(12) F. Krollpfeiffer, *et al.*, *Ber.*, **58**, 1654 (1925). This paper was first pointed out to us by J. F. Bunnett, whom we thank.



Xa: Z = S, R = CH_3
b: Z = O, R = H



Va (Partial structure)

tion was run essentially as described by Krollpfeiffer, but using Va rather than Xa. Further, treatment of Xa with sodium acetate in acetic acid gave a coupling product, unlike our results with Va and the same reagents. Simultaneously with Krollpfeiffer's paper on Xa, a paper was published by F. Arndt, *et. al.*,[13] in which the preparation of the bromochromanone Xb is described. However, the yield of Xb is said to be very poor, because it readily undergoes spontaneous dehydrohalogenation in most solvents. The dehydrobromination product then adds bromine, to give the dibromo compound analogous to VI as well as what appears to be a brominated dimer, during the bromination. If the dimeric materials reported in reactions of Xa and of Xb have the structures indicated, they could be formed by displacement of bromine from one molecule of, for example, Xb by the anion of a second molecule of the same Xb. Thus at least the thiochromanone Xa and possibly the chromanone Xb undergo displacement reactions more readily than does our admittedly more complex dihydroquinolone Va. That such comparisons should be made with caution however, is indicated by our bromination of the phenoxazine IVb. In preliminary experiments this could not be brominated to a clean-cut product. Since a really satisfactory method of making IVb in quantity is not available, as it is for IVa (*vide infra*), any report on the chemistry of IVb will have to be deferred, except for a mention of the probability that bromination of the benzene rings, which does not appear to occur to an appreciable extent in the bromination of IVa, is one of the complicating factors in the bromination of IVb.

We have given, as part of the Experimental section, procedures for the preparation of the ketone IVa. The procedure for the cyanoethylation of phenothiazine is essentially that of Smith[14] modified in minor details. The modifications, which were suggested by the late Mr. Everett Lang of our development laboratories, make it a less dangerous and exciting reaction to run. Hydrolysis of the cyanoethyl product was done by methods in the literature without modification.

The cyclization of IIIa to IVa by means of trifluoroacetic anhydride in benzene is modelled on cyclizations of some related compounds given in a patent.[15] We have used proportionately less of the relatively expensive trifluoroacetic anhydride than is used in the examples given. The patent method gave no yield. We have found that the procedure, as given here, results in a nearly quantitative yield of essentially pure IVa, and so is far superior to the cyclization of IIIa using phosphorus pentoxide which we and others had previously used.

(13) F. Arndt, *et al.*, *Ber.*, **58**, 1612 (1925).
(14) N. L. Smith, *J. Org. Chem.*, **15**, 1125 (1950).
(15) P. N. Craig and J. J. Lafferty, U. S. Patent 2,919,271. *Cf.* R. J. Ferrier and J. M. Tedder, *J. Chem. Soc.*, 1435 (1957).

Experimental

10-(2-Cyanoethyl)phenothiazine.—A suspension of 100 g. (0.5 mole) of sublimed phenothiazine in 155 ml. of commercial acrylonitrile in a 4-l. beaker was warmed to 35°. This was stirred with a thermometer as a commercial 38% solution of benzyltrimethylammonium hydroxide was added cautiously, pausing after every few drops. When the thermometer reading started to rise slowly, the addition of base was stopped. With the reagents used by us, this required at different times 3–7 ml. of the basic solution. The solution now spontaneously heated itself to the boiling point in a few seconds, and refluxed on the walls of the beaker. When the initial reaction had subsided, the solution, from which product usually started crystallizing if it were allowed to cool, was heated for an additional hour. The product was then separated by neutralizing the quaternary hydroxide with carbon dioxide immediately after addition of acetone, filtering, and adding water to the hot filtrate. The product crystallized in a first crop of 78 g. of platelets of m.p. 156–158° (lit. m.p. 158–159°) and a second crop of 10 g., m.p. 154–155°, which could be readily recrystallized from acetone–water if necessary.

10-(2-Carboxyethyl)phenothiazine (IIIa).—This was prepared by base-catalyzed hydrolysis of the nitrile, by the method in the literature.

2,3-Dihydro-3-keto-1*H*-pyrido[3,2,1-*kl*]phenothiazine (IVa).—A mixture of 100 g. (0.37 mole) of 10-(2-carboxyethyl)phenothiazine, 400 ml. of dry benzene and 80 g. (0.38 mole) of trifluoroacetic anhydride was heated under reflux and stirred on a steam bath for 5 min. It was then poured into cracked ice. The benzene solution was washed with aqueous sodium carbonate, acidification of which led to recovery of 2.5 g. of starting acid. The benzene was filtered to free it from suspended water and distilled to dryness. The resulting yellow solid residue was recrystallized from *ca.* 1 l. of absolute ethanol, giving a first crop of 76.3 g. and a second crop of 10.5 g., totaling 93%, m.p. 111–113°.

2-Bromo-3-keto-2,3-dihydro-1*H*-pyrido[3,2,1-*kl*]phenothiazine (Va).—A solution of 2.53 g. (10 mmoles) of 2,3-dihydro-3-keto-1*H*-pyrido[3,2,1-*kl*]phenothiazine (IVa) in 50 ml. of hot carbon tetrachloride was cooled to 50° and 17.5 ml. of a carbon tetrachloride solution containing 1.75 g. (11 mmoles) of bromine was added with stirring during about 30 sec. Hydrogen bromide was evolved copiously, and an oil precipitated. The latter crystallized after the reaction mixture had been heated on the steam bath for 7 min., and weighed 1.86 g. It was recrystallized from 350 ml. of nitromethane for analysis, yielding platelets of essentially the same melting point, approximately 266–270°. As might be anticipated, melting points were not always reproducible, melting point as high as 282° being readily obtained by rapid heating.

Anal. Calcd. for $C_{15}H_{10}BrNOS$ (mol. wt., 332.23): C, 54.08; H, 3.04. Found: C, 54.23; H, 2.98.

3-Keto-1*H*-pyrido[3,2,1-*kl*]phenothiazine (Ia).—A suspension of 4.60 g. (13.8 mmoles) of the bromo ketone Va in 200 ml. of glacial acetic acid was stirred at 30° with 4.2 g. (51 mmoles) of reagent grade sodium acetate for 10 min. The resulting homogeneous solution was heated at 60° overnight, filtered from a little black solid, and evaporated to dryness on the steam bath at the water pump. Titration showed that a water extract of the residue had 98% of the theoretical amount of bromide ion. The residue weighed 3.37 g. (97%) and had m.p. 206°, raised to 207° admixed with a known sample of m.p. 207.3–208°. It was recrystallized from ethyl acetate and had the same melting point and infrared absorption as the known sample. The known sample was prepared by treatment of the same bromo ketone Va suspended in ether, with ethereal dimethylamine, and had the correct elemental analysis for C and H. Melting points reported for this ketone have been 207–209°[2] and 204°.[3]

2,3-Dibromo-2,3-dihydro-3-keto-1*H*-pyrido[3,2,1-*kl*]phenothiazine (VI).—Most of 11.32 g. (45 mmoles) of 3-keto-1*H*-pyrido-[3,2,1-*kl*]phenothiazine was dissolved in 1100 ml. of boiling ethyl acetate, and a solution of 10 g. (62.5 mmoles) of bromine in 150 ml. of carbon tetrachloride was added at once. Much orange precipitate formed. The reaction was heated to the boiling point on the steam bath with stirring, cooled slightly, and filtered. The insoluble residue was 17.00 g., and a first crop of orange needles from the filtrate was an additional 2.17 g., totaling 103%. Two-gram portions could be recrystallized from 1-l. of dry ethyl acetate to give orange needle-like prisms,

melting point about 160–163°, which liberated iodine from an aqueous iodide solution acidified with acetic acid. An additional recrystallization dropped the melting point to 146–*ca.* 159°.

Anal. Calcd. for $C_{15}H_9Br_2NOS$ (mol. wt., 411.06): C, 43.61; H, 2.21. Found: C, 43.37; H, 2.72.

2-Bromo-3-keto-1*H*-pyrido[3,2,1-*kl*]phenothiazine (VII).—When an attempt was made to recrystallize the preceding 2,3-dibromo-2,3-dihydro-3-keto-1*H*-pyrido[3,2,1-*kl*]phenothiazine (VI) from nitromethane on the steam bath, the initially orange-colored solution lightened almost immediately to yellow, and became strongly acidic. After about 15 min. at 80–100°, the solution was cooled and scratched, giving yellow platelets of m.p. 144–146°, raised to 145–147.3° on recrystallization.

Anal. Calcd. for $C_{15}H_8BrNOS$ (mol. wt., 330.21): C, 54.61; H, 2.44. Found: C, 54.93, 55.00; H, 2.53; 2.48.

Acknowledgment.—The author wishes to thank Professor N. Cromwell for a stimulating discussion. Analyses were done by Dr. S. Blackman and his staff.

Studies on Condensed Systems of Aromatic Nitrogenous Series. XXII. Structural Studies of β-D-Ribofuranosylimidazopyridines[1]

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3-Methyl-3*H*-imidazo[4,5-*b*]pyridine (I), 1-methyl-1*H*-imidazo[4,5-*b*]pyridine (IV), 1-methyl-1*H*-imidazo[4,5-*c*]pyridine (II), and 3-methyl-3*H*-imidazo[4,5-*c*]pyridine (III) have been prepared. Spectroscopic comparison of a pair of isomers of methyl imidazo[4,5-*b*]pyridines (I and IV) with a nucleoside resulting from condensation of mercuric chloride complex of imidazo[4,5-*b*]pyridine with 2,3,5-tri-*O*-benzoyl-D-ribofuranosyl chloride (followed by debenzoylation) suggests that the supposed 1-β-D-ribofuranosyl-1*H*-imidazo[4,5-*b*]pyridine is 3-β-D-ribofuranosyl-3*H*-imidazo[4,5-*b*]pyridine. A nucleoside obtained from 1*H*-imidazo[4,5-*c*]pyridine by an analogous reaction was assigned the 3-β-D-ribofuranosyl-3*H*-imidazo[3,4-*c*]pyridine structure on the basis of spectral comparison with a pair of methylimidazo[4,5-*c*]pyridines.

The synthesis of nucleosides of purines or related heterocyclic bases by condensation reactions is often beset with more than one possibility for the position of attachment of the sugar moiety to the aglycon. In such cases, proof is required for this positional assignment. One technique commonly employed for such proof is to compare the ultraviolet absorption at properly selected pH values of the nucleoside product with appropriate alkyl derivatives of the aglycon.[2,3]

This technique of structural elucidation often makes use of the generally accepted empirical rule: first, in purine ring systems, 7-alkyl substituted purines have the absorption maximum at a longer wave length than corresponding 9-alkyl substituted purines.[4] Secondly, replacement of the alkyl group by a glycosyl moiety would be expected to produce little or no change in the ultraviolet absorption spectrum. Thus, adenosine (9-β-D-ribofuranosyladenine) has an ultraviolet absorption spectrum very similar to that of 9-methyladenine, but not to that of 7-methyladenine,[5] while 7-α-D-ribofuranosyladenine has almost the same absorption maximum as 7-methyladenine.[6] Both of these 7-substituted adenines possess maxima at longer wave lengths than the 9-substituted isomers.[6]

A survey of the literature, however, revealed that the first part of the empirical rule does not always hold, at least in the case of purines possessing no substituents in the pyrimidine moiety. For example, the ultraviolet absorption maximum of 7-methylpurine in cationic form appears at a shorter wave length than that of the cationic form of 9-methylpurine. Yet both have almost identical absorption maxima in their neutral form.[7]

The main purpose of the present investigation is to examine the ultraviolet absorption properties of N-substituted imidazopyridines, with emphasis being laid upon the critical examination of the utility of the aforementioned empirical rule[4] for structural elucidation in the imidazopyridine ring system.

For this purpose, 3-methyl-3*H*-imidazo[4,5-*b*]pyridine (I), 1-methyl-1*H*-imidazo[4,5-*c*]pyridine (II), 3-methyl-3*H*-imidazo[4,5-*c*]pyridine (III), and 1-methyl-1*H*-imidazo[4,5-*b*]pyridine (IV) were required among which I, II, and III have not been described in the literature. Therefore, methods of unambiguous syntheses of these compounds have been devised.

3-Methyl-3*H*-imidazo[4,5-*b*]pyridine (I) was prepared according to two different routes (see Flow Sheet 1). 3-Amino-2-methylaminopyridine (X) was prepared essentially according Schickh, Binz, and Schulz.[8] X was subjected to ring closure with formamidine acetate[9] to I. An improved synthesis of I was obtained when formic acid was employed as condensing agent. For purification, I was converted to its picrate, m.p. 203–203.5°, which, after recrystallization, was converted to I, m.p. 76–78°. I was also prepared by treatment of 1*H*-imidazo[4,5-*b*]pyridine (XIII)[10] with dimethyl sulfate in nitromethane in the presence of acetic acid. After removal of the solvent, conversion of the product to its picrates, followed by fractional recrystallization from aqueous ethanol gave two different picrates, m.p. 203–203.5° and 189–191°. One of them, m.p. 203–203.5°, was found to be identical with that of 3-methyl-3*H*-imidazo[4,5-*b*]pyridine (mixture melting point and infrared absorption spectral comparison). The other picrate was 1-methyl-1*H*-imidazo[4,5-*b*]pyridine (IV). IV was also prepared essentially according to Chatterji,

(1) Part XXI of this series, K. Adachi, *Chem. Pharm. Bull.*, **7**, 479 (1959).

(2) J. Baddiley, "Nucleic Acids," Vol. 1, E. Chargaff and J. Davidson, Ed., Academic Press Inc., New York, N. Y., 1955, pp. 143, 152.

(3) J. M. Gulland, R. E. Holiday, and T. F. Macrae, *J. Chem. Soc.*, 1639 (1934).

(4) J. M. Gulland and L. F. Story, *ibid.*, 692 (1938).

(5) J. M. Gulland and E. R. Holiday, *ibid.*, 765 (1936).

(6) W. Friedrich and K. Bernhauer, *Chem. Ber.*, **89**, 2507 (1956).

(7) A. Bendich, P. J. Russell, and J. J. Fox, *J. Am. Chem. Soc.*, **76**, 6073 (1954).

(8) O. v. Schickh, A. Binz, and A. Schulz, *Ber.*, **69**, 2593 (1936).

(9) E. C. Taylor and W. A. Ehrhart, *J. Am. Chem. Soc.*, **82**, 3138 (1961).

(10) V. Petrov and J. Saper, *J. Chem. Soc.*, 1389 (1948).