

[CONTRIBUTION FROM THE LOW-TEMPERATURE TAR LABORATORY, BRANCH OF BITUMINOUS COAL, BUREAU OF MINES]

## Infrared Spectral-Structural Correlations of Quinolines

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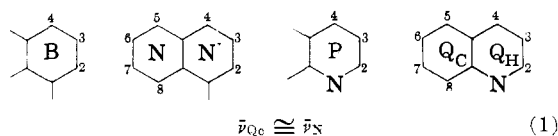
Relationships for the out-of-plane hydrogen deformation vibrations in benzenes, naphthalenes, pyridines and quinolines have been proposed for study. In general, the frequencies for quinoline carbocyclic rings may have the relationship shown in equation 1, and in most instances the frequencies for quinoline heterocyclic rings may have the relationship shown in equation 2. In 43 out of 50 cases the frequencies obtained with these equations and the observed frequencies showed agreements ranging from very good to fair, but in 7 instances the agreements ranged from poor to very poor. This could have been due to improper band assignments or poor spectra in some instances, but probably in other instances these discrepancies indicated that a different relationship exists than is shown in the equations. When the carbocyclic and heterocyclic rings of a quinoline each have the same number of adjacent hydrogens, two separate absorption bands are calculated from the equations and apparently are also always observed. Nine different polymethylquinolines were synthesized, and their infrared spectra are presented.

The occurrence of strong absorption bands, originating in the out-of-plane deformation vibrations of hydrogens on aromatic rings, in the approximate region between 900 and 700  $\text{cm}^{-1}$ , is a well-established phenomenon that has been thoroughly reviewed by Bellamy.<sup>1</sup> He points out (p. 236) that, although he could locate infrared spectra of only six quinolines in the literature, these appeared to fall in line very well with the expected absorption pattern for aromatics in general. Apparently no other reference to quinolines existed until a recent Japanese publication by Shindo and Tamura,<sup>2</sup> which was not available to the authors until the present work was nearly completed. For the correlations with the general aromatic pattern they considered the carbocyclic and heterocyclic rings separately, in the same manner as Bellamy; that is, the possibility of bands arising from vibrational interaction of adjacent hydrogens on the carbocyclic and heterocyclic rings was not discussed. They go farther than Bellamy in pointing out that when bands originating from the heterocyclic ring are compared with the bands of a pyridine with the same hydrogen structure the quinoline band is "always" at slightly higher frequency.

The present authors desired to obtain spectral-structural correlations of quinolines that might aid in the characterization of high-boiling, low-temperature, bituminous coal tar base distillate fractions consisting of polymethylquinolines. There are well over 100 isomeric possibilities, with very few published spectra, and no practical possibility of synthesizing all of the compounds. Nine quinolines were synthesized to supplement the few spectra available from the literature.

As mentioned before, Shindo and Tamura<sup>2</sup> have observed that there is a shift to greater frequencies in going from pyridines to quinoline heterocyclic rings with the same hydrogen structures. This is, of course, due to the fact that a benzene ring has been fused to the pyridine ring in the 2,3-position, replacing two adjacent alkyl substituents. The same phenomenon can be observed in going from benzenes to naphthalenoid benzene rings with the same hydrogen structures; *i.e.*, replacing two adjacent alkyl substituents with a fused benzene ring shifts the frequency to a greater value. When benzenes (B), naphthalenoid benzene rings (N'), pyri-

dines (P) and quinoline heterocyclic rings (Q<sub>H</sub>), all of the same hydrogen structures, are considered it is observed that the frequency increase in going from benzenes to naphthalenes is about the same as the frequency increase in going from pyridines to quinolines. In addition, when naphthalenoid benzene rings (N) and quinoline carbocyclic rings (Q<sub>C</sub>), with the same hydrogen structures are considered, the frequencies are about the same. These relationships appear reasonable and are best evaluated by examination of the pertinent frequencies, as shown later. It is therefore proposed that these relationships, as expressed in the following two equations, are worth studying as a possible means of better understanding the similarities that may exist among benzenes, naphthalenes, pyridines and quinolines.



with hydrogens in the same positions in Q<sub>C</sub> and N

$$\bar{\nu}_{Q_H} \cong \bar{\nu}_P + (\bar{\nu}_{N'} - \bar{\nu}_B) \quad (2)$$

with hydrogens in the same positions in Q<sub>H</sub>, P, N' and B.

To examine these equations it was necessary to collect as many spectra of benzenes, naphthalenes, pyridines and quinolines as possible. The API series of hydrocarbon spectra<sup>3</sup> was the main source for spectra of benzenes and naphthalenes. Mosby has published the spectra of nine different polymethylnaphthalenes.<sup>4</sup> Shindo and Ikekawa list the frequencies of bands for 18 methyl- and 8 ethylpyridines.<sup>5</sup> The infrared spectra of 13 different alkylpyridines were kindly donated by Glenn L. Cook.<sup>6</sup> Shindo and Tamura give the infrared spectra of all 7 monomethylquinolines.<sup>2</sup> Nisbet and Pryde present the infrared spectra of 2,3-, 2,4-, 2,6- and 2,7-dimethylquinoline.<sup>7</sup> The infrared spectra of 9 of the quinolines synthesized for the present work are

(3) "Catalog of Infrared Spectra," American Petroleum Institute Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pa.

(4) W. L. Mosby, *THIS JOURNAL*, **74**, 2564 (1952).

(5) H. Shindo and N. Ikekawa, *Pharm. Bull. (Japan)*, **4**, 192 (1956).

(6) Petroleum and Oil-Shale Experiment Station, Bureau of Mines, Laramie, Wyo.; *cf.* G. L. Cook and F. M. Church, *J. Phys. Chem.*, **61**, 458 (1957).

(7) H. B. Nisbet and A. M. Pryde, *J. Inst. Fuel*, **27**, 58 (1954).

(1) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 54 and 232.

(2) H. Shindo and S. Tamura, *Pharm. Bull. (Japan)*, **4**, 292 (1956).

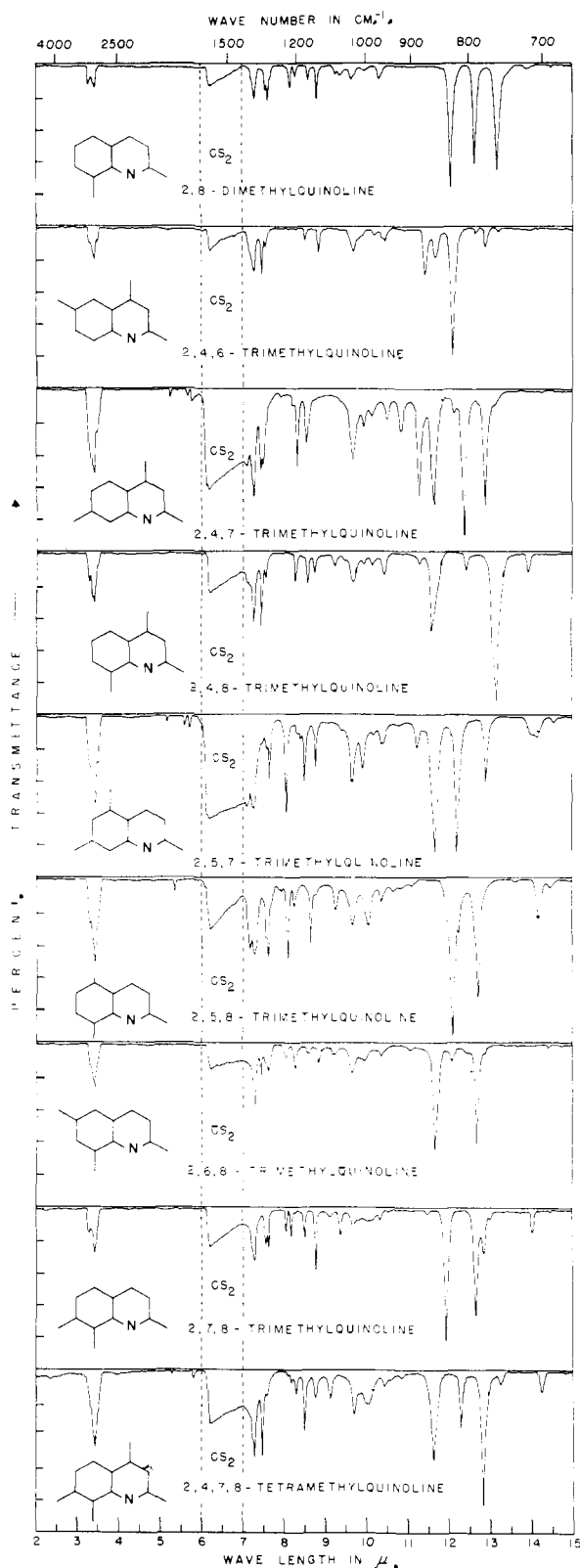


Fig. 1.—Infrared spectra of synthesized polymethylquinolines.

presented in Fig. 1. A sample of 2,3,8-trimethylquinoline was kindly donated by H. L. Lochte.<sup>8</sup>

(8) H. L. Lochte, Department of Chemistry, The University of

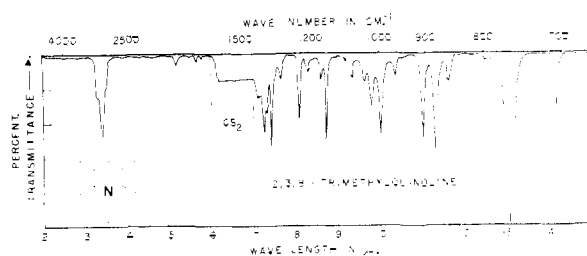


Fig. 2.—Infrared spectrum of donated sample of 2,3,8-trimethylquinoline.<sup>8</sup>

The infrared spectrum of this sample was obtained and is presented in Fig. 2.

Using the above-mentioned spectra, observed values for the frequencies of B, N, N', P, Q<sub>C</sub> and Q<sub>H</sub> were obtained, and these are all presented in Table I so that they may be readily available for the study of possible relationships.<sup>9</sup>

In most instances assignment of the bands to a specific number of hydrogens was straightforward. In these, only a few major bands occur in the 900 to 700  $\text{cm}^{-1}$  region, as can be seen, for example, in Fig. 1. Bellamy's ranges<sup>1</sup> for the different numbers of hydrogens in aromatic compounds were used as a guide in making these assignments. In a few instances there were bands of approximately equal probability for a certain assignment, and in these whichever major band agreed better with the various pertinent correlations was chosen. A few errors may have been made in band assignment.

In some instances infrared spectra were available for the naphthalenes that correspond exactly in structure to the quinolines. In others, it was necessary to use one naphthalene for the N ring and another naphthalene for the N' ring. In two instances for the N' ring the required naphthalene spectra could not be located, namely, for 1,2,3- and 1,2,4-trimethylnaphthalene. In these, satisfactory estimates of the two missing single hydrogen frequencies were obtained as follows: A number of naphthalenes were chosen that approximate one of the missing naphthalenes in structure and have single hydrogens. The benzenes that have the same structures as the naphthalene rings with the single hydrogens were then located, and the frequency differences were obtained for each pair, as indicated by the term in parentheses in eq. 2. The average difference was obtained and added to the single hydrogen frequency for the benzene, or benzenes, with the same hydrogen structure as the missing N' ring.

Using eqs. 1 and 2, calculated values for the frequencies of Q<sub>C</sub> and Q<sub>H</sub> were obtained, and these are recorded in Table I so that ready comparisons with observed values can be made. With very few exceptions, the following relationships can be seen

Texas, Austin, Texas; cf. H. L. Lochte and W. H. Meyer, *This Journal*, **78**, 2150 (1956).

(9) Two tables, (1) the frequencies and intensities of all bands in the 900 to 700  $\text{cm}^{-1}$  region for all of these compounds, and (2) the compounds used to obtain each observed frequency listed in Table I, have been deposited as Document number 5711 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting in advance \$1.25 for photoprints or \$1.25 for 35 mm. microfilm payable to: Chief, Photoduplication Service, Library of Congress.

TABLE I  
 INFRARED ABSORPTION BANDS FOR OUT-OF-PLANE HYDROGEN DEFORMATION VIBRATIONS OF METHYLQUINOLINES

Methyl-quinoline	Hydrogen		B	N	N'	P	Frequencies, cm. <sup>-1</sup>		Q <sup>c</sup>	Q <sup>u</sup>
	Number	Position					Obsd.	Calcd.		
2-	2	3, 4	804		808	817			817	821
	4	5, 6, 7, 8		743			742	743		
3-	1	2 and 4	849		861	876			888	888
	4	5, 6, 7, 8		746			752	746		
4-	2	2, 3	804		824	815			836	835
	4	5, 6, 7, 8		754			754	754		
5-	3	2, 3, 4	766		784	784			799	802
	3	6, 7, 8		810			813	810		
6-	3	2, 3, 4	766		784	784			794	802
	1	5		870			874	870		
	2	7, 8		816			830	816		
7-	3	2, 3, 4	766		775	784			799	793
	1	8		870			885	870		
	2	5, 6		824			828	824		
8-	3	2, 3, 4	766		765	784			788	783
	3	5, 6, 7		815			818	815		
2,3-Di	1	4	862		871	893			898	902
	4	5, 6, 7, 8		739			740	739		
2,4-Di-	1	3	862		871	857			856	866
	4	5, 6, 7, 8		739			743	739		
2,6-Di-	2	3, 4	804		808	817			828	821
	1	5		883			876	883		
	2	7, 8		810			807	810		
2,7-Di-	2	3, 4	804		808	817			835	821
	1	8		883			877	883		
	2	5, 6		792			770	792		
2,8-Di-	2	3, 4	804		808	817			829	821
	3	5, 6, 7		791			791	791		
2,3,8-Tri-	1	4	862		871	893			907	902
	3	5, 6, 7		769			764	769		
2,4,6-Tri-	1	3	862		882	857			875	877
	1	5		853			857	853		
	2	7, 8		810			826	810		
2,4,7-Tri-	1	3	862		882	857			885	877
	1	8		861			860	861		
	2	5, 6		810			808	810		
2,4,8-Tri-	1	3	862		871	857			862	866
	3	5, 6, 7		752			761	752		
2,5,7-Tri-	2	3, 4	804		808	817			819	821
	1	6 and 8		861			858	861		
2,5,8-Tri-	2	3, 4	804		808	817			818	821
	2	6, 7		824			830	824		
2,6,8-Tri-	2	3, 4	804		808	817			829	821
	1	5 and 7		861			859	861		
2,7,8-Tri-	2	3, 4	804		808	817			838	821
	2	5, 6		808			791	808		
2,4,5,8-Tetra-	1	3	862		871	857			857	866
	2	6, 7		824			818	824		
2,4,7,8-Tetra-	1	3	862		871	857			860	866
	2	5, 6		808			815	808		

to hold for the observed frequencies when the identical hydrogen structures are considered:  $Q_H > P > B < N'$ . Two of these relationships have been discussed previously; the fact that the pyridine frequencies are greater than the frequencies of benzenes with the same hydrogen structures has

been mentioned, but not elaborated on, by Cannon and Sutherland.<sup>10</sup>

When the observed  $Q_C$  frequencies are compared with the calculated  $Q_C$  frequencies and the observed

(10) C. G. Cannon and G. B. M. Sutherland, *Spectrochim. Acta*, **4**, 373 (1951).

TABLE II  
 PREPARATION OF SOME POLYMETHYLQUINOLINES

Compound	°C.	B.p.	Mm.	$n_D$	$t$ , °C.	Picrate, m.p., °C.	Anal. of quinoline, %			
							Calcd.	H	C	Found
2,5,8- <sup>a</sup>	143-145	15	1.5941	21	177-178.5	84.17	7.65	84.12	7.69	
	250.4	746								
2,8- <sup>b</sup>	89-90	2	1.5999	20	183	84.04	7.05	84.24	7.09	
	249.1	740								
2,6,8- <sup>c</sup>	94-95	1.27	....		185-186.5	84.17	7.65	84.34	7.80	
	267.4	746								
2,5,7	107-108	1.2	1.5980	20	204.5-205.5 d.	84.17	7.65	84.35	7.60	
	286.6	746								
2,7,8-	144-146	15	M.p. 41°		186	84.17	7.65	84.20	7.64	
	276.1	740								
2,4,7- <sup>d</sup>	116-117.5	2	1.6000	20	229.5-231 d.	84.17	7.65	84.09	7.72	
	282.9	742								
2,4,6- <sup>e</sup>	286.9	742	M.p. 41.5°		191.5-192.5	84.17	7.65	81.58	7.81	
2,4,8- <sup>f</sup>	275.8	740	M.p. 42°		192.5-193.0	84.17	7.65	84.18	7.67	
2,4,7,8-	295.5	742	M.p. 30°		180-180.5 d.	84.28	8.16	84.26	8.28	

<sup>a</sup> B.p. 144-146° at 15 mm.,  $n_D^{25}$  1.5958; picrate m.p. 181-182° (ref. 12). <sup>b</sup> B.p. 93-95° at 2 mm., R. H. F. Manske, L. Marion and F. Leger, *Can. J. Research*, **20B**, 133 (1942); b.p. 245-252° at 760 mm., B. I. Ardashev, *Zhur. Obshchei Khim.*, **19**, 550 (1949);  $n_D^{20}$  1.6022, picrate m.p. 183°, I. Heilbron and H. M. Bunbury, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1953, Vol. 2, p. 340; Vol. 4, p. 641. <sup>c</sup> B.p. 266-267° at 780 mm., picrate m.p. 185° (Heilbron). <sup>d</sup> B.p. 103-104° at 1.5 mm. (ref. 14), b.p. 280-281° at 760 mm. (Heilbron);  $n_D^{20}$  1.5997 (ref. 14); picrate m.p. 232° dec. (Heilbron). <sup>e</sup> B.p. 287° at 758 mm., O. Kruber and L. Rappen, *Chem. Ber.*, **81**, 483 (1948); m.p. 43-45°, E. Roberts and E. E. Turner, *J. Chem. Soc.*, 1832 (1927); picrate m.p. 189° (Heilbron). <sup>f</sup> B.p. 280° at 746 mm., m.p. 42°, picrate m.p. 193° (Heilbron).

$Q_H$  frequencies compared with the calculated  $Q_H$  frequencies, for the identical hydrogen structures (*i.e.*, for the same individual quinoline), they are seen to agree well in most instances. In 27 out of 50 instances the above-mentioned comparisons showed differences ranging from 0 to 5  $\text{cm}^{-1}$ , which is very good agreement. As a practical example of what a discrepancy of 5  $\text{cm}^{-1}$  would involve, one would be doing quite well to interpret the frequency values of the absorption peaks in the quinoline spectra presented by Nisbet and Pryde<sup>7</sup> to the nearest 5  $\text{cm}^{-1}$ , since 5  $\text{cm}^{-1}$  on their frequency abscissas is equal to only 0.25 mm. In 16 out of 50 instances the differences ranged from 6 to 10  $\text{cm}^{-1}$ , which should be considered fair agreement, but in 3 instances the differences ranged from 11 to 15  $\text{cm}^{-1}$ , which is poor agreement, and in 4 instances the differences ranged from 16 to 22  $\text{cm}^{-1}$ , which is very poor agreement. Therefore, there is a significant number of instances in which the relationships that have been proposed for study are not in agreement with the observed frequencies. This could be due in part to improper band assignments or inaccurate spectra, but probably in other instances these discrepancies indicate that a different relationship exists than is shown in the equations. This may imply that all of these relationships are more complex than can be visualized at the present time. It is believed by the authors that some clues to a better understanding of these relationships may be made available by a thorough examination of the spectral-structural correlations of isoquinolines. This is not possible at the present due to the lack of a sufficient quantity of isoquinoline spectra.

In general the frequency of the heterocyclic band is greater than that of the carbocyclic band, for the same number of adjacent hydrogens. This is what would be expected from the fact that the py-

ridine frequencies are greater than the benzene frequencies for the identical hydrogen structures.

As pointed out before, Shindo and Tamura<sup>2</sup> did not discuss the possibility of bands originating from vibrational interaction of adjacent hydrogens on the carbocyclic and heterocyclic rings. They do state, however, that some additional bands that cannot be interpreted appear in many cases.

#### Experimental<sup>11</sup>

**Synthesis of Quinolines.**—2,8-Dimethylquinoline, 2,5,7-trimethylquinoline, 2,5,8-trimethylquinoline, 2,6,8-trimethylquinoline and 2,7,8-trimethylquinoline were all synthesized according to the general procedure outlined by Bowen and co-workers for preparation of the 2,5,8-isomer.<sup>12</sup> The 2,5,7- and 2,7,8-isomers apparently have not been reported previously. The "Handbook"<sup>13</sup> lists 2,5,7-trimethylquinoline, m.p. 43°, very soluble in water, whereas the pure 2,5,7-isomer was found to be liquid at room temperature and essentially insoluble in water, as are the other known trimethylquinolines. Since 2,5,7-trimethylquinoline is not listed in "Chemical Abstracts, Beilstein," etc., it was assumed that the "Handbook" entry probably is in error.

2,4,6-Trimethylquinoline, 2,4,7-trimethylquinoline, 2,4,8-trimethylquinoline, 2,4,5,8-tetramethylquinoline and 2,4,7,8-tetramethylquinoline all were synthesized according to the general procedure outlined by Adams and Campbell for preparing the 2,4,7-isomer.<sup>14</sup> In this procedure the intermediate imine is prepared and purified. 2,4,7,8-Tetramethylquinoline and its imine precursor 4-(2,3-dimethylbenzimidino)-pentan-2-one, both apparently are previously unreported.

The method of Adams and Campbell for the 2,4,7-isomer had to be modified for the 2,4,6-, 2,4,8- and 2,4,7,8- isomers in that the sulfate of the quinoline was isolated by pouring the cyclodehydration reaction mixture onto cracked ice and collecting the precipitate. If the sulfate was not isolated before neutralization, no quinoline was obtainable.

(11) Microanalyses by Schwarzkopf Microanalytical Laboratory, 56-19 37th Ave., Woodside 77, N. Y.

(12) D. M. Bowen, R. W. Belfit, Jr., and R. A. Walsler, *THIS JOURNAL*, **75**, 4307 (1953).

(13) C. D. Hodgman, editor, "Handbook of Chemistry and Physics," 37th ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1954, p. 1142.

(14) R. Adams and J. Campbell, *THIS JOURNAL*, **72**, 1021 (1950).

In attempting to prepare the 2,4,5,8-isomer the cyclodehydration procedure of Adams and Campbell yielded neither the quinoline nor its sulfate when applied to the appropriate imine. However, it was observed that, by slowly distilling the imine, a slightly higher boiling fraction was obtained at the end of the distillation, which formed colorless crystals upon cooling. This material proved to be the quinoline in an impure state and had been formed in small yield by cyclodehydration induced solely by heating the imine around 110° at about 1 mm. pressure. Recrystallization from 95% ethanol gave white crystals of the quinoline, which still contained large amounts of the imine. Further purification was not successful. By comparing the infrared spectra of the imine, and the quinoline contaminated with imine, the following wave lengths, in microns, were determined to be characteristic of the quinoline: 11.67(m), 12.23(s), 12.69-(m), 12.77(m) and 14.25(m).

4-(2,3-Dimethylbenzimidino)-pentan-2-one, apparently previously unreported, consisted of white crystals, m.p. 88.0° (*Anal.* Calcd. for C<sub>13</sub>H<sub>17</sub>NO: C, 76.81; H, 8.43. Found: C, 76.92; H, 8.45.)

The physical constants of the synthesized polymethylquinolines are listed in Table II.

**Infrared Spectra of Quinolines.**—A Perkin-Elmer model 21 spectrophotometer, equipped with sodium chloride optics, was used to obtain the spectra. The slit opening at 2.0 μ was 3 μ, on Resolution Schedule 927. Under these conditions, good resolution with an acceptable noise level was obtained. Matched 0.498-mm. sodium chloride cells were used. An average concentration of about 1.0% quinoline in Baker analyzed carbon disulfide was used in obtaining the infrared spectra.

**Acknowledgments.**—The authors are indebted to Theodore L. Yarboro of this Laboratory for purification of some quinolines and determination of all atmospheric boiling points, to Glenn L. Cook for infrared spectra of alkylpyridines, and to A. L. Lochte for a trimethylquinoline sample.<sup>15</sup>

(15) Presented before the Division of Organic Chemistry, American Chemical Society, San Francisco, Calif., April, 1958.

MORGANTOWN, W. VA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

## The Action of Heterocyclic N-Oxides on 2-Bromopyridine. Oxidative Brominations Involving N-Oxide Hydrobromides

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The action of pyridine-1-oxide and of the three isomeric picoline-1-oxides on 2-bromopyridine was investigated. The main products of these reactions have the skeleton of 1-(2'-pyridyl)-2-pyridone, in which the pyridone moiety is derived from 2-bromopyridine and the pyridyl group is derived from the N-oxide. The 1-(2'-pyridyl)-3-bromo-2-pyridones and the 3,5-dibromoanalogs also isolated under certain conditions were shown to originate from secondary oxidative brominations involving the N-oxide hydrobromides,  $\begin{matrix} (+) & (-) \\ \text{N} & \text{---} & \text{OHBr} \end{matrix}$ . It is suggested that this manifestation of the oxidative power of heterocyclic N-oxides:  $\begin{matrix} (+) & (-) \\ \text{N} & \text{---} & \text{OYN} \end{matrix} \rightarrow \begin{matrix} \text{N} & \text{---} & \text{NOY} \end{matrix}$  may play a wider role in N-oxide chemistry.

Nucleophilic attack on heterocyclic systems by heterocyclic N-oxides<sup>2</sup> would open attractive synthetic possibilities.<sup>3</sup> This type of reaction is implicit in a recent report by Takeda, Hamamoto and Tone.<sup>4</sup> These authors obtained 1-(2'-pyridyl)-2-pyridone (III), pyridine and a substance C<sub>10</sub>H<sub>7</sub>ON<sub>2</sub>Br (m.p. 129°) of unknown structure, from the reaction of pyridine 1-oxide (I) with 2-bromopyridine (II) at 100°. Pyridine 1-oxide was found to react also with 2-bromoquinoline<sup>4</sup> and, later,<sup>5,6</sup> the reaction was extended to quinoline 1-oxide.<sup>7</sup> No satisfactory reaction mechanism was advanced.

We have studied<sup>1</sup> the reaction of pyridine 1-oxide and of the three isomeric picoline 1-oxides with 2-bromopyridine. The reactions were carried

out: (1) in the absence of solvent and (2) in toluene solution containing a small amount of hydrogen bromide. In the absence of solvent and of initiator, the reactions were explosively exothermic after a relatively long induction period at 100°. The induction period was virtually eliminated by the initial addition of small amounts of mineral acid. Small amounts of free radical inhibitors did not seem to influence the reaction, but the presence of piperidine had a marked inhibitory effect. No reaction was detected between 2,6-lutidine 1-oxide and 2-bromopyridine.

In our hands, the reaction of pyridine 1-oxide (I) with 2-bromopyridine (II) at 100° yielded 1-(2'-pyridyl)-2-pyridone (III) and 1-(2'-pyridyl)-3-bromo-2-pyridone (V) in about equal amounts (each in 20–30% yield). The reaction also produced pyridine and traces of 2-pyridone (VI). Compound V appeared to be identical with the bromo compound reported by Takeda.<sup>4</sup>

In toluene solution with hydrogen bromide-acetic acid catalyst, the N-oxide and the bromopyridine reacted smoothly to give 1-(2'-pyridyl)-2-pyridone (III) in 53% yield. No bromo compound V or pyridine could be detected under these conditions.

The reaction between 2-bromopyridinium hydrobromide (II·HBr, prepared separately) and pyridine 1-oxide (I), proceeded as expected, without

(1) From part of the Ph.D. Thesis of P. W. von Ostwalden; preliminary communication in *Chemistry & Industry*, 46 (1957).

(2) For a recent review see A. R. Katritzky, *Quart. Revs.*, **10**, 395 (1956).

(3) Nucleophilic attack on alkyl halides by heterocyclic N-oxides has been known for some time; see, e.g., M. Henze, *Ber.*, **70**, 1270 (1937).

(4) K. Takeda, K. Hamamoto and H. Tone, *J. Pharm. Soc. Japan*, **72**, 1427 (1952); *C. A.*, **47**, 8071 (1953).

(5) K. Takeda and K. Hamamoto, *ibid.*, **73**, 1158 (1953); *C. A.*, **48**, 12748 (1954).

(6) See also, K. Hamamoto and T. Kubota, *ibid.*, **73**, 1162 (1953); *C. A.*, **48**, 12748 (1954).

(7) The present investigation suggests that the substance C<sub>10</sub>H<sub>9</sub>ON<sub>2</sub>Br isolated by Takeda and Hamamoto<sup>4</sup> from the reaction of quinoline 1-oxide with 2-bromopyridine is 1-(2'-quinoly1)-3-bromo-2-pyridone.