[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE COLLEGE OF ARTS AND SCIENCES OF THE UNIVERSITY OF LOUISVILLE]

Pyrimidine N-Oxides and Their Infrared Absorption Characteristics

BY RICHARD H. WILEY AND STEPHEN C. SLAYMAKER

RECEIVED OCTOBER 11, 1956

The infrared spectra for several pyridines and pyrimidines and their N-oxides have been analyzed. Structural correlations and assignments have been made for the C–H stretching and C–H planar deformations and the ring vibrations in the parents. The N-oxides show a strong band at 1255–1300 cm.$^{-1}$ assigned to the N–O stretching frequency. A second band, also characteristic of the N-oxides, appears at 847–872 cm.$^{-1}$. Evidence for the hydrogen bonding of the N-oxide with proton donors is observed in the infrared spectra of the N-oxides in which a band near 2960 cm.$^{-1}$ appears in chloroform but not carbon tetrachloride solutions. This has been correlated with shifts in the ultraviolet absorption maxima of the N-oxides in solvents of varying donor ability.

Although a few pyrimidine N-oxides have been described in the recent literature,[1,2] the possibility of utilizing pyrimidine N-oxides in substitution and rearrangement reactions similar to those which have been developed for the pyridine N-oxides[3,4] warrants additional study of this class of compounds. We have prepared and characterized the previously unknown N-oxides of pyrimidine and its 2-methyl, 5-methyl and 2,4,6-trimethyl derivatives. The infrared spectra of these along with that of the known 4-methylpyrimidine N-oxide[1,2] and pyridine and the picoline N-oxides have been obtained. This report will present the results of these studies.

The pyrimidines were obtained in over-all yields of 43–51% from the palladium-on-charcoal[5,6] reductive dehalogenation of dichloropyrimidines obtained in turn from the corresponding dihydroxy compounds. The N-oxides, described in Table I, were prepared using hydrogen peroxide in glacial acetic acid as described previously[3] for the preparation of pyridine N-oxides although in somewhat lower yields (11–36%). The highly deliquescent nature of the pyrimidine N-oxides coupled with their tendency to sublime *in vacuo* requires that they be handled carefully.

As a preliminary to a consideration of the infrared spectra of the N-oxides, we have evaluated the assignments for a number of the ring vibrations in the pyridines and pyrimidines listed in Table II. The vibrational spectrum of pyridine itself has been fully discussed in the literature.[7,8] As compared to benzene, the introduction of nitrogen into the ring changes the symmetry group from D_{6h} to C_{2v}, with the result that the doubly degenerate benzene ring vibrations are split. The loss of one atom in the benzene–pyridine comparison also requires that three fundamental vibrations be absent in pyridine. Pyrimidine belongs to the symmetry point group C_{2v} also, and although few changes would be expected in the ring vibrations, the loss of three more fundamentals—one C–H stretching, one C–H planar deformation and one C–H out of plane deformation—would be expected. In accordance with this, pyridines normally show two bands in the aromatic C–H stretching region and the pyrimidines show only a single, rather sharp band at 3048 cm.$^{-1}$. Furthermore, the solution spectrum of pyridine clearly shows four medium strength bands (1214, 1144, 1068, 1031 cm.$^{-1}$) in the region where planar hydrogen deformations might be expected and only three bands appear in the same region in pyrimidine (1221, 1155, 1070 cm.$^{-1}$). The third band expected to be lost is a species A_2 C–H out-of-plane deformation which would be inactive in the infrared spectrum of pyridine. The ring vibrations from substituted pyrimidines, with no hydroxyl or amino substituents, have previously been assigned to single absorption bands at 1580–1520 and 990 cm.$^{-1}$.[9] For pyrimidine itself further correlations have been made[9,10] which agree for the most part with those found in this Laboratory.

Assignments for the ring vibrations, v1, v8a, v8b, v19a and v19b[11] for pyridine, the picolines and eight pyrimidines are given in Table II. The location of the v8 and v19 pairs of ring deformation vibrations appears to be quite characteristic, with a slight shift to lower frequencies in both pairs of vibrations in going from the pyridines to the pyrimidines and another shift to still lower frequencies upon chlorine substitution on the pyrimidine ring. The intensities of these four vibrations vary widely, but at least one band in each pair is strong in all of the compounds studied. The v1 band, which can be thought of as a ring "breathing" vibration, appears in the range 1001–986 cm.$^{-1}$ in 10 of the 12 compounds studied.

The spectra of several tertiary amine oxides have been reported by Mathis-Neol[12] who examined five compounds and placed the absorption of the N–O stretching vibration in the range 970–950 cm.$^{-1}$. Goubeau and Fromme[13] have assigned a band at 947 cm.$^{-1}$ in the Raman spectra of one compound to this vibration. Ito and Hata[14] have assigned a band at 832 cm.$^{-1}$ to the N–O

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[1] E. Ochiai, M. Ishikawa and S. Zai-Ren, *J. Pharm. Soc. Japan*, **67**, 34 (1947).

[2] E. Ochiai and H. Yamanaka, *Pharm. Bull.* (*Japan*), **3**, 175 (1955).

[3] E. Ochiai, *J. Org. Chem.*, **18**, 534 (1953).

[4] F. E. Cislak, *Ind. Eng. Chem.*, **47**, 800 (1955).

[5] N. Whittaker, *J. Chem. Soc.*, 1646 (1953).

[6] C. G. Overberger and I. C. Kogon, THIS JOURNAL, **76**, 1881 (1954).

[7] C. H. Kline and J. Turkevich, *J. Chem. Phys.*, **12**, 300 (1944).

[8] L. Corrsin, B. J. Fox and R. C. Lord, *ibid.*, **21**, 1170 (1953).

[9] L. N. Short and H. W. Thompson, *J. Chem. Soc.*, 168 (1952).

[10] I. A. Brownlie, *ibid.*, 3062 (1950).

[11] The numbering system of the normal vibrational modes of benzene first introduced by E. B. Wilson (*Phys. Rev.*, **45**, 706 (1934) is used here. This convenience has been arbitrarily adopted by the earlier workers in the study of pyridine.[7,8]

[12] Mme. Raymonde Mathis-Noel, M. M. Robert Wolf and Fernand Gallois, *Compt. rend.*, **242**, 1873 (1956).

[13] J. Goubeau and L. Fromme, *Z. anorg. Chem.*, **258**, 18 (1949).

[14] M. Ito and N. Hata, *Bull. Chem. Soc. Japan*, **28**, 353 (1955).

TABLE I

PYRIMIDINE N-OXIDES

N-Oxide substituent	M.p.,[a] °C.	M.p. $HgCl_2$[b] complex, °C.	Yield, %	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
	85–88C	....	11			29.16[c]	28.98 29.22
2-Methyl	*ca.* 50D	165–169M	31	15.73[d]	15.83 15.90	1.59	1.70 1.74
4-Methyl[e]	78–79C	146–147W	31			25.44[e]	25.08 25.10
5-Methyl	113–116C	170–170.5W	36	15.73[d]	15.79 15.69	1.59	1.65 1.60
2,4,6-Trimethyl[f]	67–72D	143.5–145W	30	15.39[g]	15.58 15.65	1.85	1.89 1.86

[a] C, recrystallized from carbon tetrachloride; D, purified by distillation and desiccation. [b] M, recrystallized from methanol; W, recrystallized from water. [c] Analysis for nitrogen. [d] As $C_5H_6N_2{\cdot}HgCl_2$ complex. 5-Methylpyrimidine N-oxide calcd. for $C_5H_6N_2O$: C, 54.54; H, 5.49; N, 25.44. Found: C, 53.94; H, 5.54; N, 24.68. [e] B.p. 110–113° (3 mm.); reported b.p. 90–110° (bath.) (0.014 mm.), m.p. 74–78°. [f] B.p. 100–102° (1 mm.). [g] As $C_7H_{10}N_2{\cdot}1.5HgCl_2$.

TABLE II[a]

ASSIGNED RING VIBRATIONS FOR PYRIDINES AND PYRIMIDINES

Compound	v8a	v8b	v19a	v19b	v1
Pyridine	1600m[b]	1582s	1484m	1441f	991m
α-Picoline	1597s	1572m	1479s	1433m	996m
β-Picoline	1597w	1580s	1479s	1416s	1029s
γ-Picoline	1605s	1563m	1497w	1416s	996m
Pyrimidine	1613w	1567s	1466m	1401s	990m
2-Methylpyrimidine	1585s	1565s	1441vs[c]	1399m	995m
4-Methylpyrimidine	1590s	1553m	1479m	1391s	998m
5-Methylpyrimidine	1585w	1563s	[d]	1410s	986w
2,4,6-Trimethyl-	1590s	1555m	[d]	1401m	992w
2,4-Dichloro-5-methyl-	1563m	1520s	1399s	1376vs	1001m
2,4-Dichloro-6-methyl-	1565s	1534s	[d]	[d]	1008w
4,6-Dichloro-2-methyl-	1555sh	1536s	1406s	1537s	1000m

[a] Values are in frequencies (cm.$^{-1}$); s = strong, m = medium, w = weak, sh = shoulder, vs = very strong. All are in carbon tetrachloride. [b] Kline and Turkevich[7] and Corrsin[8] assign the 8a and 8b vibrations in pyridine in a slightly different manner. They find a difficultly resolvable doublet at 1570–1580 cm.$^{-1}$ which they attribute to the v8a and v8b vibrations. They find also a band at 1597 cm.$^{-1}$ which they attribute to a combination tone strengthened by resonance with the v8 vibrations. These studies were conducted in the gas phase and in pure liquid pyridine. It would seem possible that the solution spectra used in our series of measurements could effect a further separation of the bands. It seems highly improbable that all of the bands in the first column can be attributed to a combination band since in γ-picoline and again in 2,4,6-trimethylpyrimidine the first band is far stronger than any other band in either spectra. [c] This extremely strong band probably involves some contribution from the asymmetric carbon hydrogen deformation bands expected in this region. The other methyl-containing compounds in this list show this to be a band of medium strength falling very near 1449 cm.$^{-1}$. The symmetric methyl deformation appears in the range 1390–1370 cm.$^{-1}$ in all of the methyl-containing compounds. [d] Bands not assigned.

stretching vibration in pyridine N-oxide on the basis that acetoxime shows an absorption in this same range which may also be attributed to an O–N stretching vibration. The absorption characteristics of the nine N-oxides studied are given in Table IV. All show an extremely strong band near 1266 cm.$^{-1}$ in carbon tetrachloride solution. For pyridine N-oxide itself and in α- and γ-picoline N-oxides this band falls at 1264–1260 cm.$^{-1}$. In β-picoline N-oxide, where the methyl group is not attached to an electron-deficient carbon, the band appears at 1290 cm.$^{-1}$. The location of this band is similar in the pyrimidine N-oxides but is often more complex. It is split into two strong bands in both 2- and 4-methylpyrimidine N-oxides. 2,4,6-Trimethylpyrimidine N-oxide shows a shift to 1255 cm.$^{-1}$. As in the case of β-picoline N-oxide, 5-methylpyrimidine N-oxide shows a shift to higher frequencies with its absorption appearing at 1300 cm.$^{-1}$. Pyrimidine N-oxide itself, although not sufficiently soluble to obtain a spectrum in carbon tetrachloride, shows a strong band at 1261 cm.$^{-1}$ in chloroform. The exact position of this band is affected by the formation of hydrogen bonds with the solvent. This has been shown to produce a shift to lower frequencies in other N-oxides. Thus, pyridine N-oxide shows the band at 1264 cm.$^{-1}$ in carbon tetrachloride and 1252 cm.$^{-1}$ in chloroform, and γ-picoline N-oxide shows the band at 1264 cm.$^{-1}$ in carbon tetrachloride and 1248 cm.$^{-1}$ in chloroform. Since chloroform itself ab-

TABLE III

THE ULTRAVIOLET SPECTRA OF γ-PICOLINE N-OXIDE IN VARIOUS SOLVENTS

Solvent	Wave length, mμ	log ε
Water[15]	256	4.155
Methanol	264.5	4.059
50 mole % $CHCl_3$ in methanol	267.5	4.261
Chloroform	276.5	4.368
Carbon tetrachloride	288	4.489

TABLE IV

PRINCIPAL ABSORPTION BANDS IN INFRARED SPECTRA OF PYRIDINE AND PYRIMIDINE N-OXIDES[a]

Pyridine	1608m, 1488sh, 1464s, 1266vs, 841s
α-Picoline	1616m, 1497s, 1462s, 1420m, 1385m, 1266vs, 856s
β-Picoline	1610m, 1567w, 1490m, 1466m, 1433m, 1389w, 1290vs, 856m
γ-Picoline[b]	1490s, 1453m, 1264s, 856m
Pyrimidine[c]	1577w, 1534m, 1468m, 1410s, 1261s, 845s
2-Me-pyrimidine	1536w, 1488m, 1431s, 1402s, 1287s, 1272s, 872s
4-Me-pyrimidine	1603m, 1565w, 1524m, 1490m, 1439s, 1416m, 1274vs, 1266vs, 858s
5-Me-pyrimidine	1582m, 1548w, 1497w, 1379s, 1300s, 858m
2,4,6-Trimethyl	1608s, 1531m, 1445s, 1416m, 1255vs, 860m

[a] Values are frequencies in cm.$^{-1}$; s = strong, m = medium, w = weak, vs = very strong, sh = shoulder. In carbon tetrachloride except as noted. [b] Owing to the limited solubility of this compound in carbon tetrachloride, only the stronger bands were visible. [c] Chloroform.

sorbs strongly near this region, the resulting loss of resolution encountered makes the assignment somewhat approximate in the case of pyrimidine N-oxide.

The strength of this band near 1266 cm.$^{-1}$ and the solvent shift have caused us to assign this band to the N–O stretching frequency in these compounds despite the previous assignments.[12–14] This need not be an inconsistency, since it is well known that other physical and chemical properties of the heterocyclic N-oxides differ greatly from those of the trialkyl amine oxides. A number of ionic resonance forms are possible in the heterocyclic N-oxides, and these would give the N–O bond considerable double bond character. The pyrimidine and pyridine N-oxides show no consistent absorption in the 950 cm.$^{-1}$ region previously stated to be characteristic of the N–O stretching vibration.

A second band which appears to be characteristic of the heterocyclic N-oxides is found near 847 cm.$^{-1}$. In pyridine N-oxide this band occurs at 841 cm.$^{-1}$, while in pyrimidine N-oxide the absorption occurs at 845 cm.$^{-1}$. All of the methyl-containing compounds show this band in the narrow range 860–855 cm.$^{-1}$ with the exception of 2-methylpyrimidine N-oxide where the band falls at 872 cm.$^{-1}$. This band is in the region tentatively assigned previously[14] to the O–N stretching vibration. Since it is not subject to the displacement in chloroform as is the 1260 cm.$^{-1}$ band, it now seems advisable to revise this assignment.

An interesting phenomena is observed in the spectra of chloroform solutions of N-oxides. A sharp and unusually strong band occurs near 2960 cm.$^{-1}$ which is absent from the spectra obtained in carbon tetrachloride solutions. This is probably due to the absorption associated with the C–H stretching vibration in chloroform which is shifted to longer wave lengths by hydrogen bonding. A number of other compounds capable of acting as donors have been shown to produce shifts in this band. Quinoline, for example, is known to produce a shift from 3067 to 2960 cm.$^{-1}$ as well as a fourfold strengthening of the absorption.[15] A shift of this magnitude would bring the chloroform frequency to a point where the compensating cell would not eliminate it, thus introducing an entirely spurious band in the N-oxide spectra. Further indication of hydrogen bonding is found in the ultraviolet spectra. Thus, the absorption band for γ-picoline N-oxide shows a strong hypsochromic shift in going from non-polar solvents to polar solvents (see Table III). It has been suggested[16] that this band arises from a $\pi \rightarrow \pi^*$ transition. This type of transition has usually been known to produce a bathochromic (red) shift under the effect of solvation.[17] Large hypsochromic (blue) shifts normally are evidence of $n \rightarrow \pi^*$ transitions,[17] but such a transition is inconsistent with the high intensity of the absorption.

In contrast with the similarities previously noted[12] between the infrared spectra of tertiary amine N-oxide and the corresponding amine, the spectra of the heterocycles and their N-oxides are not greatly similar. While pyridine, pyrimidine and their methyl derivatives show characteristic ring vibrations which are strong and easily assigned, the N-oxides show much less regularity. There is a striking weakening of absorption below 1490 cm.$^{-1}$ as compared to the parent compounds. A number of the bands found in these N-oxides are listed in Table IV. Although the spectrum of pyrimidine shows many resemblances to that of pyridine, the spectra of the N-oxides show fewer resemblances between the two ring systems.

Acknowledgment.—The authors wish to express their appreciation for a grant from the National Science Foundation (Grant NSF-G1918) in support of this research.

Experimental

Details of typical procedures are given in the following paragraphs. Complete data are given in Table I. Combustion analyses were performed by Micro Tech Laboratories, Skokie, Ill.

The pyridine, picolines and their N-oxides used in the spectroscopic studies were generously furnished by Reilly Tar and Chemical Co. These compounds were redistilled or recrystallized before use. The tetraethoxypropane was generously donated by Carbide and Carbon Chemical Co. and was used as received.

5-Methylpyrimidine.—Forty-eight grams (0.3 mole) of 4,6-dichloro-5-methylpyrimidine was divided into three portions of 16.0 g., and each portion was hydrogenated in a Parr hydrogenation apparatus with 10.0 g. of powdered magnesium oxide and 2.0 g. of 5% palladium-on-charcoal catalyst in 300 ml. of 50% aqueous methanol. From an initial pressure of about 50 pounds the theoretical amount of hydrogen was absorbed smoothly in 90 minutes. The filtered solution was poured into 1500 ml. of hot water containing 180 g. of mercuric chloride. The thick white precipitate was collected on a filter after cooling, then was dried and placed in a 2000-ml. distilling flask containing 600 ml. of water and 85 g. of sodium sulfide. After removal of 400 ml. of distillate, saturation with sodium hydroxide caused the amine layer to form. This layer was separated and the aqueous solution extracted with three 80-ml. portions of ether. The combined ether fractions and the amine were dried over calcium sulfate, concentrated to 40 ml. and distilled. After removing a small amount of ether, a rather large forerun was collected (b.p. 80–150°), followed by the methylpyrimidine, b.p. 150–155°. The forerun was dried over potassium hydroxide and redistilled to give more of the crude methylpyrimidine. Redistillation gave 15.5 g. (55%) of 5-methylpyrimidine, b.p. 152–154° (760 mm.). The clear, colorless liquid solidified on chilling, m.p. 28–30°; reported[18] b.p. 151.5° (735 mm.), m.p 30.5°.

Other pyrimidines were prepared similarly: pyrimidine (48% from uracil), b.p. 121–123° (760 mm.), n^{23}_{D} 1.4983 (reported[8] b.p. 123–124° (762 mm.); 2-methylpyrimidine (43% from 2-methyl-4,6-dihydroxypyrimidine), b.p. 129–133° (760 mm.), n^{26}_{D} 1.4878 (reported[19] b.p. 130–131° (750 mm.); 4-methylpyrimidine (51% from 4-methyluracil), b.p 139–141° (760 mm), n^{29}_{D} 1.4918 (reported[6] b.p. 141–145° (760 mm.), n_D 1.4940). 2,4,6-Trimethylpyrimidine was prepared in 26% yield from acetamidine and acetylacetone,[20] b.p. 84–87° (45 mm.). The direct condensation of tetraethoxpyropane with acetamidine in hydrochloric acid saturated ethanol gave only a 2% yield of 2-methylpyrimidine isolated as the mercuric chloride complex.

2,4,6-Trimethylpyrimidine N-Oxide.—Six and one-tenth grams (0.05 mole) of 2,4,6-trimethylpyrimidine was heated with 30 ml. of glacial acetic acid and 8 ml. of 30% hydrogen peroxide at 70° for 5 hr. Six additional ml. of peroxide was

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(15) A. M. Buswell, W. H. Rodebush and M. F. Roy, THIS JOURNAL, **60**, 2528 (1938).

(16) H. H. Jaffé, *ibid.*, **77**, 4451 (1955).

(17) G. J. Brealey and M. Kasha, *ibid.*, **77**, 4462 (1955).

(18) O. Gerngross, *Ber.*, **38**, 3396 (1905).

(19) R. G. Jones, E. C. Kornfeld and K. C. McLaughlin, THIS JOURNAL, **72**, 3539 (1950).

(20) A. Bowman, *J. Chem. Soc.*, 494 (1937).

added and the temperature maintained for 16 hr. Evaporation to 10 ml., addition of 20 ml. of water and evaporation again to 10 ml. gave a yellow oil which was saturated with sodium carbonate and extracted with five 20-ml. portions of chloroform. The chloroform extracts were dried with calcium sulfate and evaporated in vacuum to leave a viscous oil. Distillation of this gave 2.3 g. of crude product, b.p. 100–102° (1 mm.), which partially solidified to white crystals in the receiver. Careful drying on a clay plate in a desiccator gave crystals, m.p. 67–72°. The product was very hygroscopic and formed a solid complex with mercuric chloride. One recrystallization of this complex from water gave crystals, m.p. 143.5–145°.

5-Methylpyrimidine N-Oxide.—Seven and five one-hundredth grams (0.075 mole) of 5-methylpyrimidine was heated at 70° for 6 hr. in 30 ml. of glacial acetic acid containing 8 ml. of hydrogen peroxide solution (30%). Eight additional ml. of peroxide was added and the heating continued for 20 hr. The resulting solution was treated as before. The crude solid from the chloroform extracts was recrystallized from carbon tetrachloride to yield white, hygroscopic crystals, m.p. 113–116°. A mercuric chloride complex, m.p. 170–170.5°, was obtained.

The infrared spectra were obtained with a Baird double beam recording spectrophotometer equipped with sodium chloride optics using 0.1-mm. sodium chloride cells. All measurements were calibrated against the 3.419 band of polystyrene. The ultraviolet spectra were obtained using a Beckman DU spectrophotometer in 1-cm. quartz cells.

LOUISVILLE 8, KENTUCKY

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Reaction of 2-Bromopyridine N-Oxides with Active Methylene Compounds

BY ROGER ADAMS AND WALTER REIFSCHNEIDER

RECEIVED NOVEMBER 10, 1956

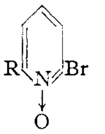
2-Bromopyridine N-oxides condense with active methylene compounds holding a carboalkoxy group to give derivatives of 2-isoxazolono[2,3-a]pyridines. These products react with aqueous alkali; the isoxazolone ring is opened and carbon dioxide is lost with formation of the 2-substituted pyridine N-oxides. 2-Carbethoxy-2-isoxazolono[2,3-a]pyridine is hydrogenated with platinum oxide catalyst to 3-carbethoxy-2-isoxazolono[2,3-a]piperidine.

The electron-attracting power of the ring nitrogen accounts for the facile attack of halogen in the 2- and 4-halopyridines by nucleophilic reagents. In spite of this reactivity, the bromine atom in 2-bromopyridine fails to respond to treatment with diethyl sodiomalonate.[1] The introduction of the malonic ester group in the 2-position of pyridine was achieved[2] by using 5-nitro-2-chloropyridine in which the halogen is further activated by the electron-withdrawing nature of the nitro group.

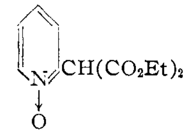
The introduction of an N-oxide into the pyridine system also is known to increase the reactivity of the 2-, 4- and 6-positions of the ring. A reaction between 2-bromopyridine 1-oxide (I) and diethyl sodiomalonate might therefore be expected. A reaction does take place between these reagents under relatively mild conditions, but diethyl 2-pyridylmalonate 1-oxide (III) is not isolated. Instead, a compound of the formula $C_{10}H_9NO_4$ results. The reaction apparently does not stop after the initial condensation but loss of ethanol occurs to form 3-carbethoxy-2-isoxazolono[2,3-a]pyridine (IV).

To demonstrate the generality of this reaction, 2-bromopyridine 1-oxide (I) and 2-bromo-6-methylpyridine 1-oxide (II) were subjected to the action of various active methylene compounds. 2-Bromo-6-methylpyridine 1-oxide (II) is a stable compound in comparison with 2-bromopyridine 1-oxide (I) and therefore was more often used in this study. Upon addition of ethyl sodioacetoacetate and ethyl sodiobenzoylacetate to 2-bromopyridine 1-oxide (I) and 2-bromo-6-methylpyridine 1-oxide (II) the expected cyclized products V, VI, IX and X were obtained.

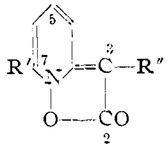
When ethyl sodiocyanoacetate was treated with 2-bromo-6-methylpyridine 1-oxide (II) and benzene was used as the solvent, three compounds were isolated, (1) 2-imino-3-carbethoxy-7-methylisoxazolo[2,3-a]pyridine (XIV), (2) 3-cyano-7-methyl-2-isoxazolono[2,3-a]pyridine (XI) and (3) ethyl [α-cyano-β-amino-β-(7-methyl-2-isoxazolono[2,3-a]pyridyl-3)]-acrylate (XII).

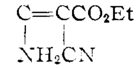


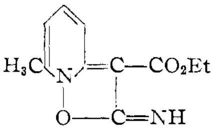
I, R = H
II, R = CH_3



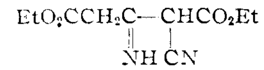
III



	R′	R″
IV,	H	CO_2Et
V,		$COCH_3$
VI,		COC_6H_5
VII,		CO_2H
VIII,	CH_3	CO_2Et
IX,		$COCH_3$
X,		COC_6H_5
XI,		CN
XII,		 $C(NH_2)=C(CN)CO_2Et$
XIII,		CO_2H



XIV



$EtO_2CCH_2C(=NH)-CH(CN)CO_2Et$

XV

The structure of the first compound XIV, a yellow product, was established by analysis ($C_{11}H_{12}N_2O_3$) and the presence in the infrared spectrum of an N–H band at 3285 cm.$^{-1}$ and a conjugated ester band at 1688 cm.$^{-1}$.

The second compound XI was a colorless product with the empirical formula $C_9H_6N_2O_2$ and showed bands in its infrared spectrum for CN at

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[1] C. S. Kuhn and G. H. Richter, THIS JOURNAL, **57**, 1927 (1935).

[2] W. Gruber and K. Schloegl, *Monatsh.*, **80**, 499 (1949); **81**, 473 (1950); W. Gruber, *Can. J. Chem.*, **31**, 1181 (1953); see also Aust. Patent 127,795 (*Chem. Zentr.*, **103**, II, 123 (1932)).