

observed by Ruhemann.¹⁶ However, only part of the recrystallized pyridone melted at 176–180°, the rest melting at 189–190°.

Cyclization of triketone Ic with methylamine to form 4-pyridone XX. Methylamine was bubbled into an ethanolic solution of 9.3 g. of triketone Ic, and the solvent was then removed on the steam bath. The oily residue was recrystallized from a mixture of benzene and hexane to give 3.9 g. (42%) of 2,6-diphenyl-1-methyl-4(1H)-pyridone (XX), m.p. 185–188° (reported⁸² m.p. 187°). The infrared spectrum in the region 5.5–6.5 μ showed a strong band at 6.16 μ , a medium band at 6.47 μ , and a weak band at 6.37 μ . Ultraviolet spectrum: $\lambda_{\max} = 237 \text{ m}\mu$, 270 $\text{m}\mu$; $\log \epsilon = 4.39, 4.26$.

A 1.8-g. sample of this compound was added to 7 ml. of acetonitrile, and a few drops of methanol were added to

dissolve all the solid. An excess (2 ml.) of methyl iodide was added, and the solution was allowed to stand overnight at room temperature. Ether was added to precipitate 1.7 g. (61%) of the methiodide of 4-pyridone XX (white crystals), m.p. 123–129° dec. The product was recrystallized by dissolving it in methanol and adding ether. Three recrystallizations changed the melting point to 129–137° dec. The infrared spectrum in the region 5.5–6.5 μ showed a strong band at 6.15 μ , and a medium band at 6.36 μ . Ultraviolet spectrum: $\lambda_{\max} = 279 \text{ m}\mu$; $\log \epsilon = 4.06$; broad shoulder at 232–239 $\text{m}\mu$; $\log \epsilon = 4.40$.

Anal. Calcd. for $\text{C}_{13}\text{H}_{13}\text{ON}$: C, 56.59; H, 4.50; N, 3.47. Found: C, 56.32; H, 4.77; N, 3.40.

DURHAM, N. C.

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

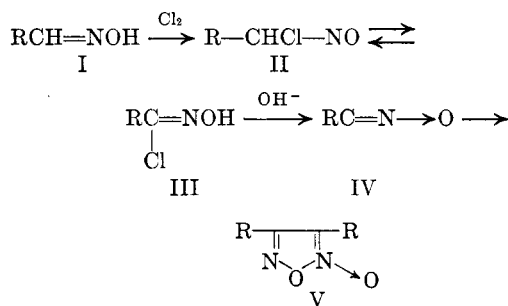
Infrared Spectra of the Nitrile *N*-Oxides: Some New Furoxans

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Received October 2, 1959

A number of aryl nitrile *N*-oxides have been prepared in carbon tetrachloride solution and their infrared spectra studied. Absorption bands at 2295 cm^{-1} and 1370 cm^{-1} characteristic of the triple bond and *N*-oxide linkages of the nitrile oxide group have been identified. Several new diaryl furoxans have been obtained by dimerization of these nitrile *N*-oxides and two new aliphatic nitrile oxides have been obtained in solution.

The nitrile *N*-oxides (IV) are somewhat unstable compounds formed by the action of dilute alkali on hydroxamic chlorides as indicated in the reaction scheme:^{1–9} and the assignment of a proper



structure has received considerable attention.^{6,10–12} They are highly reactive toward olefinic linkages

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to form isoxazoles¹³ and they dimerize readily to furoxans⁵ (V). Because of the ease with which they dimerize very little is known about their physical properties. A few appropriately substituted types; e.g., *p*-chlorobenzonitrile *N*-oxide, dimerize slowly and the physical properties of these compounds have been studied.^{12,14,15} Others, such as benzonitrile *N*-oxide, dimerize rapidly during isolation and are difficult to characterize. The lowest molecular weight recorded^{6,7} for benzonitrile *N*-oxide is 134, whereas theory requires 119, indicating that partial dimerization occurs before the molecular weight can be determined.

We have now devised a procedure for recording the spectra of the less stable nitrile *N*-oxides in carbon tetrachloride solution. The nitrile *N*-oxides were prepared from the hydroxamic chlorides obtained by the route given above. The oximes were prepared by standard methods¹⁶ and were chlorinated at 0° in 8*N* hydrochloric acid¹⁷ or in organic solvents. The hydroxamic chlorides were not purified as the melting points of the crude products agreed well with recorded values. The hydroxamic chlorides were dissolved or suspended in carbon

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tetrachloride at 0° and the solutions were shaken with dilute icecold aqueous sodium hydroxide or sodium carbonate. The carbon tetrachloride layers were separated, dried at 0°, and used for the spectroscopic studies. The nitrile *N*-oxides thus prepared are listed in Table I. The identities of the nitrile *N*-oxides were confirmed, in most cases, by isolating the furoxans formed on standing. Strongly electron-donating substituents in the aromatic nucleus facilitated chlorination of the ring with the result that *o*-methoxybenzaloxime gave 5-chloro-2-methoxybenzoxime nitrile *N*-oxide and salicylaloxime gave 3,5-dichloro-2-hydroxybenzoxime nitrile *N*-oxide. In order to confirm these structures, *o*-methoxybenzaldehyde and salicylaldehyde were chlorinated to give 5-chloro-2-methoxybenzaldehyde and 3,5-dichloro-2-hydroxybenzaldehyde respectively. The oximes from these aldehydes gave the same furoxans as those from *o*-methoxybenzaldehyde and salicylaloxime. 2,4-Dimethoxybenzaloxime gave a solution of a nitrile *N*-oxide but no pure furoxan could be obtained and it is probable that a mixture of chlorinated products was formed.

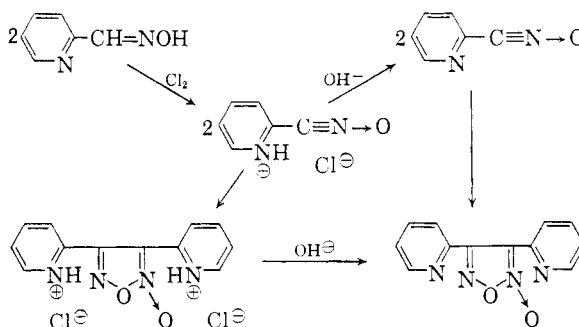
TABLE I

INFRARED ABSORPTION OF NITRILE *N*-OXIDES IN CARBON TETRACHLORIDE

<i>N</i> -oxide	Maxima ^a
Benzonitrile <i>N</i> -oxide	2288s, 1712m, 1368vs, 1098s, 1029w, 835w
<i>p</i> -Phenylbenzoxime nitrile <i>N</i> -oxide ^b	2294, 1376, 1211, 1103, 836
<i>p</i> -Methylbenzoxime nitrile <i>N</i> -oxide	2294m, 1704m, 1616w, 1368s, 1253w, 1208w, 1182w, 1098m, 850m
<i>o</i> -Nitrobenzoxime nitrile <i>N</i> -oxide ^b	2304, 1536, 1393, 1346, 1121, 1070, 857,
<i>m</i> -Nitrobenzoxime nitrile <i>N</i> -oxide ^b	2294, 1546, 1391, 1357, 1134
<i>m</i> -Chlorobenzoxime nitrile <i>N</i> -oxide	2288s, 1595w, 1567m, 1422m, 1370vs, 1235w, 1126m, 1088m, 999w, 964w, 880w
<i>p</i> -Chlorobenzoxime nitrile <i>N</i> -oxide	2294s, 1597m, 1495m, 1374vs, 1100vs, 1016m, 935m, (826s) ^c
2,4-Dichlorobenzoxime nitrile <i>N</i> -oxide	2299, 1590, 1391, 1372, 1124, 1100, 1045, 873
5-Chloro-2-methoxybenzoxime nitrile <i>N</i> -oxide	2294m, 1486s, 1464m, 1414m, 1366w, 1346m, 1287w, 1274w, 1253w, 1125m, 1107w, 1075m, 1027m, 902w, 803w
3,5-Dichloro-2-hydroxybenzoxime nitrile <i>N</i> -oxide ^b	2299, 1704, 1672, 1471, 1422, 1353, 1326, 1163, 870
2,3-Dichloro-2-methylbutyronitrile <i>N</i> -oxide	2294vs, 1733w, 1460m, 1385s, 1168w, 1131m, 1071s
4,5-Dichloro-2,2-dimethylpentanonitrile <i>N</i> -oxide	2288s, 1721s, 1460s, 1401m, 1393s, 1236s, 1211m, 1152s

^a Frequencies in cm.⁻¹. Intensities indicated by the abbreviations w (weak), m (medium), s (strong), vs (very strong). ^b Dilute solution. Intensities of bands not estimated. ^c Partly obscured by solvent absorption.

The extreme readiness with which hydrogen chloride is eliminated from hydroxamic chlorides is demonstrated by the behavior of oximes containing basic groups. On chlorination, *p*-dimethylaminobenzaloxime, pyridine-2-aldoxime, and pyridine-4-aldoxime gave white solids, insoluble in organic solvents and very soluble in water. The aqueous solutions were acid to litmus and gave an immediate precipitate with silver nitrate solution. When aqueous solutions of these substances were made alkaline at 0°, nothing was extracted from the solution with carbon tetrachloride. If the aqueous phases were allowed to stand, the furoxans were formed. If the white solids were allowed to stand and then treated with alkali, the furoxans were again obtained. It is postulated that the hydroxamic chlorides are formed only momentarily from oximes containing basic groups and that the white solid product obtained is the hydrochloride of the nitrile *N*-oxide. Addition of alkali gives the water-soluble nitrile *N*-oxide which forms the furoxan on standing. Alternatively, the hydrochloride dimerizes on standing and addition of alkali liberates the furoxan. These reactions are formulated for pyridine-2-aldoxime:



A carbon tetrachloride solution of benzenedinitrile *N*-oxide was not obtained by treating *p*-benzenedihydroxamic chloride (from terephthalaloxime) with alkali. The dinitrile *N*-oxide was apparently insoluble in carbon tetrachloride and rapidly formed a high molecular weight polymeric product presumably having alternating benzene and furoxan rings in the chain.

The frequencies and approximate intensities of the principal infrared absorption bands of the carbon tetrachloride solutions of the nitrile *N*-oxides are recorded in Table I. Carbon tetrachloride and chloroform were considered the most suitable solvents for this study. Since it has been noted¹⁸ that the hydrogen atom in chloroform may interact with *N*-oxides, carbon tetrachloride was used. In some cases the nitrile *N*-oxides were only sparingly soluble in carbon tetrachloride. The following infrared absorption bands have been recorded¹⁴ for three comparatively stable nitrile *N*-oxides in carbon tetrachloride: 2,4,6-trimethylbenzoxime

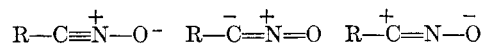
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N-oxide, 2287 cm.⁻¹, 1348 cm.⁻¹; 2,3,5,6-tetramethylbenzotrile *N*-oxide, 2288 cm.⁻¹, 1346 cm.⁻¹; *p*-chlorobenzotrile *N*-oxide, 2292 cm.⁻¹, 1377 cm.⁻¹ (cf. Table I).

In some cases (benzotrile *N*-oxide, *p*-methylbenzotrile *N*-oxide, 3,5-dichloro-2-hydroxybenzotrile *N*-oxide, and the two aliphatic compounds), bands near 1710 cm.⁻¹ indicated that the solutions were contaminated by traces of aldehyde which may have been formed by hydrolysis of the oximes by hydrochloric acid during the chlorination stage. No other impurities have been detected. Traces of oxime or of unreacted hydroxamic chloride would have been extracted by alkali and the furoxans were almost completely soluble in carbon tetrachloride.

All the nitrile *N*-oxides give a strong and remarkably constant band near 2295 cm.⁻¹; the slight variations in frequency are not significantly larger than the experimental error. Absorption in the 2300 cm.⁻¹ to 2100 cm.⁻¹ region is characteristic of triple bond stretching vibrations. Acetylenes absorb at 2140–2100 cm.⁻¹ (monosubstituted) or 2260–2190 cm.⁻¹ (disubstituted; often very weak).¹⁹ Nitriles absorb at 2260–2240 cm.⁻¹ (saturated aliphatic), 2240–2220 cm.⁻¹ (aromatic) or 2235–2215 cm.⁻¹ (α,β -unsaturated aliphatic).¹⁹ Azides absorb at 2160–2120 cm.⁻¹¹⁹ and acid azides give two peaks between 2250 cm.⁻¹ and 2140 cm.⁻¹.²⁰ The only other compounds with peaks in this region are the isocyanates which absorb at 2275–2263 cm.⁻¹.²¹ Although nitrile *N*-oxides absorb close to the region of triple bond stretching for other compounds, their absorption is at a significantly higher frequency. This band is therefore regarded as highly characteristic of the aryl nitrile *N*-oxides. The frequency difference between the nitrile *N*-oxides and the isocyanates is not large but is still significant and the nitrile *N*-oxides and the isocyanates may be distinguished by other features of their infrared spectra. A band near 1350 cm.⁻¹ was attributed¹⁴ to N—O stretching vibrations. Vibrations of this type have been reported over a wide range of frequencies. Pyridine *N*-oxides give one or two strong bands between 1300 cm.⁻¹ and 1235 cm.⁻¹ (as high as 1319 cm.⁻¹ in one case) in carbon tetrachloride^{22,23} or in chloroform.^{24,25} Pyrimidine *N*-oxides show a strong band in the range 1300 cm.⁻¹ to 1255 cm.⁻¹.¹⁸ Within these ranges the frequencies vary considerably for different ring substituents. For the furoxans, a

doublet in the range 1475–1410 cm.⁻¹ has been attributed to the *N*-oxide group and a band in the 1360–1300 cm.⁻¹ region is regarded as being due to a ring N—O vibration.²⁶ The *N*-oxides of tertiary aliphatic amines absorb at 970–950 cm.⁻¹.²⁷ It seems clear that the absorption frequency of the *N*-oxide function depends greatly on the nature of the N—O bond and may lie anywhere between the normal N—O single bond stretching frequency (near 900 cm.⁻¹²⁸) and the normal N:O double bond stretching frequency (1621 cm.⁻¹ to 1488 cm.⁻¹).³ It has been shown, indeed, that a graph of N—O stretching frequency against N—O bond length gives a smooth curve.³ All the nitrile *N*-oxides we have studied have a strong absorption band near 1370 cm.⁻¹. In most cases this is the strongest band in the spectrum. The frequency of this absorption is near the upper end of the range for N—O stretching vibrations and this fact suggests that the N—O bond in the nitrile *N*-oxides must possess considerable double-bond character. The hybridization of the bonds in the nitrile *N*-oxides is illustrated by the three possible electronic structures:



The last structure, involving a large charge-separation, would be expected to contribute little to the hybrid although it becomes significant in addition reactions. The second structure, however, may make a large contribution to the hybrid. The infrared spectrum of the nitrile *N*-oxides is clearly correlated with the accepted structure for these compounds. It was not possible to correlate the position of the 1370 cm.⁻¹ band with the nature of the nuclear substituents. When strongly electron-donating substituents were present in the original oxime, the nucleus of the resulting nitrile *N*-oxide was chlorinated. It may be significant, however, that the band occurred at the highest frequencies (over 1390 cm.⁻¹) in the nitrobenzotrile *N*-oxides.

The 1370 cm.⁻¹ band is less useful for identification of the nitrile *N*-oxide group than that at 2290 cm.⁻¹ as many other groups give bands in this region. The high intensity of the band increases its usefulness, however, and distinguishes the nitrile *N*-oxides from the isocyanates which give a very strong band at 2275–2263 cm.⁻¹ but only a weak band near 1370 cm.⁻¹.³ The unexpected nature of the isocyanate spectrum is accounted for by mechanical coupling of the C:N and C:O stretching vibrations.^{14,29}

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The other bands in the infrared spectra of the nitrile *N*-oxides may be correlated with known structural features of the nucleus and the substituents. The exception is the strong band near 1100 cm^{-1} given by several of the compounds studied. Bands in the range 1225–950 cm^{-1} have been correlated with the out-of-plane deformation vibrations of the nuclear hydrogen atoms in substituted benzenes.¹⁹ Such bands are usually weak and it seems unreasonable to assign the strong 1100 cm^{-1} band to such a structural feature. The band is particularly prominent in the spectra of *p*-substituted benzonitrile *N*-oxides and it also appears in the aliphatic types. We have not at present correlated this band with any molecular vibration.

The procedures outlined for the preparation of the aryl nitrile *N*-oxides has been applied to two new aliphatic types. It is recognized that the reactions involved cannot be successfully accomplished with aliphatic aldehydes having α -hydrogen atoms.⁷⁻⁹ Trimethylacetone nitrile *N*-oxide is the only aliphatic nitrile *N*-oxide known and its infrared spectrum has been recorded.¹⁵ We have converted tiglic aldoxime to 2,3-dichloro-2-methylbutyronitrile *N*-oxide and 2,2-dimethyl-4-pentenaldoxime to 4,5-dichloro-2,2-dimethylpentanonitrile *N*-oxide. Characteristic infrared absorption bands were observed at 2294 cm^{-1} and 1385 cm^{-1} for the former and 2288 cm^{-1} and 1393 cm^{-1} for the latter. Neither of these nitrile *N*-oxides nor their furoxans were isolated in an analytically pure form. The carbon tetrachloride solutions of the *N*-oxides showed only traces of carbonyl and no olefinic absorption in accordance with the structures assigned but indicative of impurities.

There is still some disagreement about the structure of the furoxans, but the 1,2,5-oxadiazole 2-*N*-oxide formulation (V) is generally used and is accepted for the present work. The chemistry of the furoxans has recently been reviewed.³⁰ Most of the furoxans prepared in the course of the present work are new compounds. Data pertaining to them are recorded in Table II. In many cases the furoxans could be prepared simply by digesting the hydroxamic chloride with excess dilute aqueous sodium hydroxide or sodium carbonate. A cleaner product was obtained by preparing a solution of the nitrile *N*-oxide in an organic solvent and allowing the solution to stand at room temperature for twenty-four to forty-eight hours. Ether was used as the solvent rather than carbon tetrachloride as the nitrile *N*-oxides were more soluble in ether. No pure furoxan could be prepared from 2,4-dimethoxybenzaldoxime. A mixture of chlorinated materials was obtained. When *o*-nitrobenzohydroxamic chloride was treated with dilute aqueous sodium carbonate at 0°, a white solid, m.p. 70–75°,

was obtained. On standing for one hour at room temperature this became brown and after standing overnight was a black tar. No pure furoxan was isolated. The solution of *o*-nitrobenzonitrile *N*-oxide was obtained normally (see above). It is known, however, that *o*-nitrobenzaldoxime undergoes unusual transformations with alkali.³¹

The infrared absorption spectra of a number of diaryl and diarylfuroxans have been studied and correlations of bands with their structural features have been made.²⁶ The spectra of the furoxans which we have prepared show features similar to those reported^{26,33} and are extremely complex.

EXPERIMENTAL

Infrared spectra were measured with a Baird recording double beam spectrometer. Melting points were measured in open capillaries and are uncorrected. Analyses were by Micro Tech Laboratories, Skokie, Ill.

Aldehydes. The aldehydes used were commercially available materials, with the exception of *p*-phenylbenzaldehyde, 5-chloro-2-methoxybenzaldehyde, and 3,5-dichloro-2-hydroxybenzaldehyde.

***p*-Phenylbenzaldehyde.** Biphenyl was formulated with carbon monoxide and hydrogen chloride in the presence of aluminum chloride and cuprous chloride.³⁴ The crude product was converted to the oxime without purification.

5-Chloro-2-methoxybenzaldehyde. *o*-Methoxybenzaldehyde (5 g.) was dissolved in chloroform (25 ml.) and chlorine was passed into the ice cold solution for 90 min. The solution was allowed to stand for 1 hr. at room temperature and the solvent was evaporated under reduced pressure. The residue was recrystallized from aqueous acetic acid to give 5-chloro-2-methoxybenzaldehyde (4 g.; 63%), m.p. 80–81° (lit.,³⁵ m.p. 81°).

3,5-Dichloro-2-hydroxybenzaldehyde. Salicylaldehyde was chlorinated as described above, to give 3,5-dichloro-2-hydroxybenzaldehyde³⁶ (65% yield), m.p. 93–94° (lit.,³⁶ m.p. 95°).

Oximes. Benzaldoxime, pyridine-2-aldoxime, and pyridine-4-aldoxime were commercially available materials. The other oximes were prepared by a standard method¹⁶ using an ethanolic solution of hydroxylamine acetate. The yields and melting points were as follows: *p*-phenylbenzaldoxime, 70% yield from biphenyl, m.p. 147–149° (lit.,³⁷ m.p. 149–150°); *p*-methylbenzaldoxime, 23%, m.p. 76–78° (lit.,¹⁶ m.p. 79°); *o*-nitrobenzaldoxime, 70%, m.p. 102–103° (lit.,³⁷ m.p. 102–103°); *m*-nitrobenzaldoxime, 82%, m.p. 125° (lit.,³⁷ m.p. 121–123°); *m*-chlorobenzaldoxime, 92%, m.p. 72–72.5° (lit.,³⁷ m.p. 70–71°); *p*-chlorobenzaldoxime, 90%, m.p. 107–109° (lit.,³⁷ m.p. 110°); 2,4-dichlorobenzaldoxime, 58%, m.p. 134–136° (lit.,³⁷ m.p. 136–137°); *p*-dimethylaminobenzaldoxime, 91%, m.p. 144–145° (lit.,³⁷ m.p. 144°); *o*-methoxybenzaldoxime, 58%, m.p. 100–101° (lit.,³⁷ m.p. 92°); 2,4-dimethoxybenzaldoxime, 83%, m.p. 107–108° (lit.,³⁸ m.p. 106°); salicylaldoxime, 50%, m.p. 62–63° (lit.,³⁷ m.p. 63°); terephthaldehydedioxime, 76%,

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TABLE II
 3,4-DIARYLFUROXANS

Ar	M.P. ^a	Formula	Analysis	
			N, Calcd.	N, Found
Phenyl	113–114 ^b			
<i>p</i> -Phenylphenyl	159–160	C ₂₆ H ₁₈ N ₂ O ₂	7.14	7.04
<i>p</i> -Methylphenyl	142–143 ^c			
<i>m</i> -Nitrophenyl	182–184 ^d			
<i>m</i> -Chlorophenyl	96–97	C ₁₄ H ₈ N ₂ O ₂ Cl ₂	9.12	9.31
<i>p</i> -Chlorophenyl	180–181	C ₁₄ H ₈ N ₂ O ₂ Cl ₂	9.12	9.19
2,4-Dichlorophenyl	159–160	C ₁₄ H ₆ N ₂ O ₂ Cl ₄	7.80	7.80
5-Chloro-2-methoxyphenyl	183–184	C ₁₆ H ₁₂ N ₂ O ₄ Cl ₂	7.70	7.70
3,5-Dichloro-2-hydroxyphenyl	195	C ₁₄ H ₆ N ₂ O ₄ Cl ₄	6.87	6.93
<i>p</i> -Dimethylaminophenyl	143–144	C ₁₈ H ₂₂ N ₄ O ₃ ^e	16.36	16.45
2-Pyridyl	169.5–170.5	C ₁₂ H ₈ N ₄ O ₂	23.33	24.11 ^f
4-Pyridyl	140–141	C ₁₂ H ₈ N ₄ O ₂	23.33	23.09

^a All the furoxans decomposed, though some only slowly, at their melting points. ^b Lit. m.p. 114–115° (ref. 32). ^c Lit. m.p. 143–144 (ref. 2). ^d Lit. m.p. 183–185 (ref. 7). ^e Including one molecule of water of crystallization. ^f The discrepancy was confirmed by a repeat analysis of another sample. The properties of this compound were otherwise normal and no explanation of this result can be offered.

m.p. 201–202° (lit.,¹⁶ m.p. 200°); 3,5-dichloro-2-hydroxybenzaldoxime, 63%, m.p. 194° (lit.,³⁶ m.p. 195°); tiglic aldoxime, 43%, m.p. 42–43° (lit.,³⁷ m.p. 43°).

5-Chloro-2-methoxybenzaldoxime was prepared in 71% yield, m.p. 139–140°.

Anal. Calcd. for C₉H₈NO₂Cl: N, 7.55. Found; N, 7.53.

2,2-Dimethyl-4-pentaldoxime, b.p. 85°/17 mm., n_D^{25} 1.4565 was prepared from 2,2-dimethyl-4-pental³⁹ in 27% yield.

Anal. Calcd. of C₇H₁₂NO: C, 66.10; H, 10.30; N, 11.01. Found: C, 65.83; H, 10.20; N, 10.95.

Nitrile N-oxides. A typical preparation of a carbon tetrachloride solution of a nitrile *N*-oxide is described. Solutions of benzonitrile *N*-oxide, *p*-phenylbenzotrile *N*-oxide, *p*-methylbenzotrile *N*-oxide, *o*-nitrobenzotrile *N*-oxide, *m*-nitrobenzotrile *N*-oxide, *m*-chlorobenzotrile *N*-oxide, *p*-chlorobenzotrile *N*-oxide, 2,4-dichlorobenzotrile *N*-oxide, and 5-chloro-2-methoxybenzotrile *N*-oxide were prepared from the corresponding oximes by this procedure. *o*-Methoxybenzaldoxime gave the same product as 5-chloro-2-methoxybenzaldoxime. Salicylaldoxime and 3,5-dichloro-2-hydroxybenzaldoxime both gave 3,5-dichlorobenzotrile *N*-oxide; sodium carbonate was used instead of sodium hydroxide for the dehydrochlorination step.

Tiglic aldoxime gave 2,3-dichloro-2-methylbutyronitrile *N*-oxide and 2,2-dimethyl-4-pentaldoxime gave 4,5-dichloro-2,2-dimethylpentanonitrile *N*-oxide identified by their infrared spectra. Attempts to isolate the products or furoxans derived from them gave only decomposition products. The infrared spectra of the nitrile *N*-oxides have been recorded in Table I.

The melting points (all with decomposition) of the crude hydroxamic chlorides were as follows: benzohydroxamic chloride, m.p. approx. 45° (lit.,¹⁷ m.p. 42–48°); *p*-methylbenzohydroxamic chloride, m.p. 68–71° (lit.,² m.p. 69–70°); *o*-nitrobenzohydroxamic chloride, m.p. 90–93° (lit.,⁴ m.p. 92–94°); *m*-nitrobenzohydroxamic chloride, m.p. 96–96° (lit.,⁴ m.p. 94–95°); *m*-chlorobenzohydroxamic chloride, m.p. 75–80°; *p*-chlorobenzohydroxamic chloride, m.p. 82–86°; 2,4-dichlorobenzohydroxamic chloride, m.p. 100–105°; 5-chloro-2-methoxybenzohydroxamic chloride, m.p. 115–125°; 3,5-dichloro-2-hydroxybenzohydroxamic chloride, m.p. 172–174°; 1,4-benzenedihydroxamic chloride, m.p. 183–186° (lit.,² m.p. 188°). The aliphatic hydroxamic chlorides were liquids.

p-Phenylbenzotrile *N*-oxide. *p*-Phenylbenzaldoxime (10 g.) was chlorinated in 8*N* hydrochloric acid (50 ml.) at

0°.¹⁷ The resulting suspension was filtered and the crude *p*-phenylbenzohydroxamic chloride (11 g.; 94%) m.p. 125–127° dec. was used for the next stage. A portion was recrystallized from cyclohexane to give pure *p*-phenylbenzohydroxamic chloride, m.p. 129–130°.

Anal. Calcd. for C₁₂H₁₀NOCl: N, 6.05. Found: N, 6.09.

p-Phenylbenzohydroxamic chloride (1 g.) was suspended in spectro-grade carbon tetrachloride (20 ml.). The suspension was cooled to 0° and 14% aqueous sodium hydroxide (6 ml.) was added dropwise with shaking. The mixture was kept at 0° and shaken occasionally for 30 min. The carbon tetrachloride layer (5 ml.) was withdrawn by means of a pipet and was allowed to stand over anhydrous calcium chloride at 0° for 30 min. The solution was used for infrared studies as quickly as possible.

Furoxans. Typical procedures for preparing the furoxans are described. Most of the furoxans could be prepared by the method used for 3,4-di(*p*-biphenyl)furoxan. The method described for 3,4-di(*m*-chlorophenyl)furoxan was more satisfactory and was used to prepare 3,4-diphenylfuroxan, 3,4-di(*p*-methylphenyl)furoxan, 3,4-di(*m*-nitrophenyl)furoxan, 3,4-di(*p*-chlorophenyl)furoxan, 3,4-di(2,4-dichlorophenyl)furoxan, 3,4-di(5-chloro-2-methoxyphenyl)furoxan and 3,4-di(3,5-dichloro-2-hydroxyphenyl)furoxan. The methods described for 3,4-di(2-pyridyl)furoxan were used also for 3,4-di(4-pyridyl)furoxan and for 3,4-di(*p*-dimethylaminophenyl)furoxan. The melting points and analyses of the furoxans are recorded in Table II.

3,4-Di(*p*-biphenyl)furoxan. *p*-Phenylbenzohydroxamic chloride (2 g.) was warmed on a steam bath with an excess of concd. aqueous sodium carbonate for 30 min. Carbon dioxide was evolved. The solution was cooled and filtered and the solid was washed with water and air dried. The crude product (1 g.; 78%), m.p. 151–153°, was recrystallized from aqueous ethanol and from benzene to give pure 3,4-di(*p*-biphenyl)furoxan, m.p. 159–160°. For analysis, see Table II.

3,4-Di(*m*-chlorophenyl)furoxan. *m*-Chlorobenzohydroxamic chloride (from 1.5 g. of *m*-chlorobenzaldoxime) was dissolved in ether (30 ml.). The solution was cooled in ice and an excess of 10% aqueous sodium hydroxide was added dropwise, with shaking. The solution was shaken occasionally for 30 min., at 0°. Sufficient ether was added to dissolve a white precipitate which formed and the ether layer was separated and dried over anhydrous sodium sulfate. The ether solution was allowed to stand for 48 hr. at room temperature, was evaporated and the residue (1 g.; 66%), m.p. 75–80°, was recrystallized from aqueous ethanol to give pure 3,4-di(*m*-chlorophenyl)furoxan, m.p. 96–97°. For analysis, see Table II.

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3,4-Di(2-pyridyl)furoxan. Pyridine-2-aldoxime (2 g.) was dissolved in 8*N* hydrochloric acid (15 ml.) at 0°. Chlorine was passed into the ice cold solution for 20 min. An excess of concd. aqueous sodium carbonate was added and the solution was warmed on a steam bath for 30 min. The solution was filtered and the brown solid was recrystallized from benzene/cyclohexane and from water to give 3,4-di(2-pyridyl)furoxan (0.5 g.; 27%), m.p. 169–170.5°. For analysis, see Table II.

Pyridine-2-aldoxime was dissolved in carbon tetrachloride or in ether, and chlorine was passed into the ice-cold solution for 20 min. The solution was filtered and the white solid was retained. The white solid was insoluble in organic solvents but soluble in water to give an acid solution.

The white solid was suspended in spectro-grade carbon tetrachloride and an excess of 10% aqueous sodium hydroxide was added to the ice-cold suspension. The mixture was allowed to stand at 0°, with occasional shaking, for 20 min. Part of the carbon tetrachloride layer was removed. The infrared spectrum of this solution showed only very weak absorption. On standing, the aqueous solution de-

posited 3,4-di(2-pyridyl)furoxan, m.p. 165–168° after recrystallization from water.

A portion of the white solid was allowed to stand at room temperature for 48 hr. It was then dissolved in water and the ice-cold solution was made alkaline. 3,4-Di(2-pyridyl)furoxan, m.p. 166–168° after recrystallization from water, was precipitated.

Acknowledgment. This investigation was completed under Contract DA-33-008-Ord-734 between the Office of Ordnance Research and the University of Louisville. The infrared spectrometer used in these studies was purchased with a grant from the Research Corporation and the Brown-Forman Company. The authors gratefully acknowledge this support. The authors thank the Tennessee Eastman Company for the gift of a sample of 2,2-dimethyl-4-pentalen.

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The Basic Strength of Pyrrole

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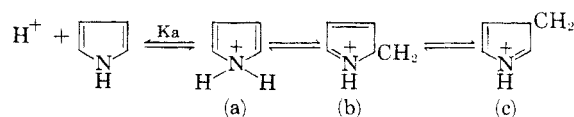
Received September 25, 1959

The pK_a of pyrrole has been determined spectrophotometrically using the Hammett H_0 indicator method and is found to be -0.27 . The problems caused by the acid-catalyzed polymerization of pyrrole have been overcome by a back-extrapolation method and a differential plot.

It has long been recognized that pyrrole is a very weak base although no reliable measurement of its pK_a value has been made. Hall¹ established a relationship between the basicity constants of a series of bases in a nonaqueous solvent and water, and showed that by titrating the bases in glacial acetic acid, the pK_a values of certain bases, which could not be determined in aqueous solutions, could be predicted. Pyrrole was dissolved in glacial acetic acid and titrated conductometrically with perchloric acid; by inspecting the titration curve obtained, the approximate pK_a of pyrrole was reported to be $+0.4$. More recently, Tamres and co-workers² found that for a series of closely related compounds there was a linear relationship between the acidity constants and the ability of these compounds to form hydrogen bonds. For a number of compounds related to pyridine it was shown that $\Delta\nu = 14.8 pK_a + 136$, where pK_a is the acid dissociation constant of the compound and $\Delta\nu$ the frequency shift in cm^{-1} of the oxygen-deuterium stretching frequency in the infrared spectrum of methyl deuterioalcohol solutions. In the presence of pyrrole, $\Delta\nu$ was 161 cm^{-1} and therefore the pK_a of pyrrole is 1.7 if the above linear relationship is applicable. However, too much reliance cannot be

placed on acid dissociation constants obtained from studies on hydrogen bonding for a number of reasons. For example, different steric and solvation effects will be involved with different pyridine bases; there is also a fundamental difference between protonation of a pyridine type molecule where electrostatic forces are primarily involved, and hydrogen bond formation with such a compound in which a covalent bond is formed.² Moreover, in most pyridine type bases protonation takes place at the nitrogen atom, whereas in pyrrole it is possible that protonation takes place at a carbon atom. If carbon protonation occurs³ the above relationship between $\Delta\nu$ and pK_a is less likely to be valid.

In spite of the fact that pyrrole is an extremely weak base a certain amount of the protonated species (a), (b), or (c) is formed when pyrrole is



added to mineral acids. The protonated ion of pyrrole is highly unstable and undergoes polymerization very readily, one of the chief products of polymerization being the trimer, 2,5-dipyr-

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