shall not offer a decision. First, the presence of so many noncoincidences may have more import than do the corresponding number of coincidences, which can[20] occur fortuitously. Second, four of the five coincidences in the ir are weak bands that might be expected to be forbidden. It is not impossible that these coincidences arise from a second conformation, although there is no discernible pattern in the alteration of their intensities in going from the solid to solution. More likely, the overabundance of coincidences points toward the weakness of this technique as a straightforward method of conformational analysis.[21]

In summary, nmr evidence is consistent with a very flattened chair or with certain boat forms in solution. The method of ir–Raman coincidences does not provide a clear choice between the alternatives in the solid. The question cannot be fully answered without X-ray evidence, which we hope to obtain in the future.

(21) The question of dimers in nitrosamines is still somewhat controversial.[8,22] By dilution experiments, we saw no evidence for dimers from the ir spectra in solution.

(22) S. D. Christian and P. Klaeboe, *Acta Chem. Scand.*, **21**, 2293 (1968).

Experimental Section

The nmr spectra were taken on Varian Model T-60 and A-60 spectrometers. Spectral analyses were carried out on the Control Data Corp. 6400 computer equipped with a Calcomp plotting accessory. The ir spectra were obtained from Beckman IR-9, IR-10, and IR-11 spectrometers. Raman spectra[23] were recorded on a Spex 1400-II double monochromator with a 6328 He–Ne laser and photon-counting detectors.

N,N′-Dinitrosopiperazine was prepared by treatment of piperazine dihydrochloride with sodium nitrite and hydrochloric acid according to the same procedures used by George and Wright.[10] The product was recrystallized from water to give cream-colored crystals, mp 156–158° (lit.[10] 156–156.5°).

Registry No.—N,N-Dinitrosopiperazine, 140-79-4.

(23) The authors are deeply grateful to Dr. D. F. Shriver and Mr. B. I. Swanson for assistance in the operation of the IR-11 and the Raman spectrometers. We also wish to thank the National Science Foundation for a departmental instrument grant that permitted purchase of the IR-11.

Oxidation of Pyridineacetic Acid Derivatives with Peracids. An Unusual α Hydroxylation

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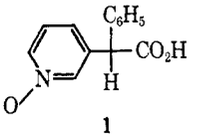
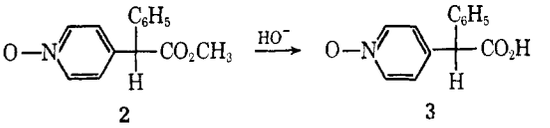
Oxidation of various isomeric methyl α-phenylpyridineacetates with peracids is described. The 3- and 4-pyridyl isomers reacted "normally" to give the corresponding N-oxides in high yields. However, with the 2-pyridyl isomer, the main product was the corresponding glycolate derivative, the net result being hydroxylation at the α carbon. Similar results were obtained with some related compounds having in common a –CHR′COR grouping at the 2 position of the pyridine ring. The second-order rate constants measured for this reaction are compared with those of peracid oxidation of olefins and pyridyl nitrogen. The much higher rate of the α oxidation as compared with oxidation of pyridine nitrogen shows that rearrangement of an initially formed N-oxide is not involved; rather, a mechanism is suggested in which the rate-determining step is epoxidation of a tautomeric form, followed by fast opening of the oxirane ring.

It is well documented that 2- and 4-pyridineacetic acids are generally less stable than their phenyl counterparts;[1,2] indeed, α-phenyl-substituted derivatives decarboxylate below room temperature.[3,4] However, the N-oxides of both α-phenyl-2- and -4-pyridineacetic acids have been prepared in high yields from reactions of the respective N-phenacetylpyridinesulfonamide 1-oxide with sodium hydroxide.[5] Since these acids or their N-oxides were needed for another study, attempts were made to prepare the latter by a more classical route: peracid oxidation of the respective esters or amides followed by hydrolysis. The 4-pyridyl derivatives were indeed successfully prepared this way; however, in the case of the 2-pyridyl isomers oxidation at the α carbon was the predominant reaction path. A study of this unusual reaction constitutes the main part of the present paper.

In contrast to its two isomers, α-phenyl-3-pyridineacetic acid could be prepared by saponification of the ester. Subsequent oxidation of the acid with peracetic acid gave the N-oxide **1** in good yield. In a similar fashion, oxidation of methyl α-phenyl-4-pyridineacetate with either peracetic acid or *m*-chloroperbenzoic acid yielded the liquid N-oxide **2**, characterized as its picrate.[5] Saponification gave the corresponding acid **3** in 85% yield. However, treatment of the 2-pyridine isomer **4** under the same conditions gave a crystal-



1



2 **3**

line product, which according to thin layer chromatography consisted of three compounds besides the starting material. Attempts to get some quantitative data as to their relative amounts using gas chromatography were unsuccessful because of decomposition.

Two of the compounds were successfully separated by chromatography on silica gel. The major product analyzed correctly for the expected N-oxide of **4**, but the infrared spectrum exhibited no significant absorp-

(1) J. C. Godfrey in "Pyridine and Derivatives," Part III, E. Klingsberg, Ed., Interscience Publishers, New York, N. Y., 1962, Chapter XI.

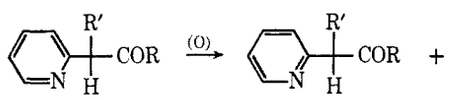
(2) W. von E. Doering and V. Z. Pasternak, *J. Amer. Chem. Soc.*, **72**, 143 (1950).

(3) D. Singh, *J. Chem. Soc.*, 2445 (1925).

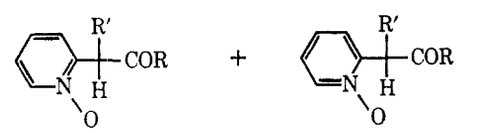
(4) L. Panizzon, *Helv. Chim. Acta*, **27**, 1748 (1944).

(5) T. Naito, R. Dohmori, and T. Kotake, *Chem. Pharm. Bull.* (Tokyo), **12**, 588 (1964); R. Dohmori, *ibid.*, **12**, 595 (1964).

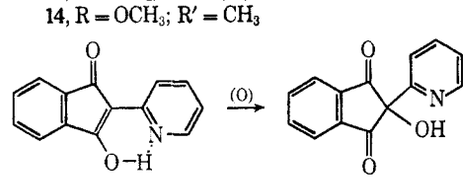
tion in the 1250-cm^{-1} region, characteristic of pyridine N-oxides;[6] absorption at 3400 cm^{-1} indicated the presence of a hydroxyl group. Saponification was followed by decarboxylation to yield phenyl-2-pyridylcarbinol (**7**) as the exclusive product. Furthermore, the nmr spectrum showed only the presence of a methyl group and aromatic protons. These data are only compatible with the structure methyl α-phenyl-2-pyridineglycolate (**5**). The second product was shown to contain four oxygen atoms, and similar evidence to that presented above suggested the N-oxide structure **6**. This was subsequently confirmed by the formation of **6** as the sole product from oxidation of **5** or **4** with 1 or 2 mol of peracid, respectively. The third product which had the longest retention time on silica gel was only present in trace amounts, and we were not able to separate any of this compound. By comparison of its retention time with those of the N-oxides **11** and **15** (*vide infra*), we assume that it is the N-oxide of **4**.



4, R = OCH_3; R′ = C_6H_5 **5**, R = OCH_3; R′ = C_6H_5
8, R = NH_2; R′ = C_6H_5 **9**, R = NH_2; R′ = C_6H_5
12, R = OCH_3; R′ = CH_3 **13**, R = OCH_3; R′ = CH_3



6, R = OCH_3; R′ = C_6H_5 **11**, R = NH_2; R′ = C_6H_5
10, R = NH_2; R′ = C_6H_5 **15**, R = OCH_3; R′ = CH_3
14, R = OCH_3; R′ = CH_3



16 **17**

Results similar to those described above for the 2-pyridyl ester were obtained by peracid oxidation of the corresponding amide. Oxidation of α-phenyl-2-pyridineacetamide (**8**) gave three products, as shown by chromatography on silica gel. The major product, obtained in 57% yield, was assigned the structure α-phenyl-2-pyridineglycolamide (**9**) on the basis of spectroscopic evidence and its conversion into the ester **5** by methanolic hydrochloride acid. The remaining products were eluted as a mixture in 29% yield. Separation of pure samples was achieved by repeated crystallizations and the components were subsequently identified as the N-oxides **10** and **11**. In the aromatic part of the nmr spectrum of **11** the proton adjacent to nitrogen in the pyridine ring appeared as a triplet at δ 8.35 as compared with a doublet at 8.58 in the parent compound. Similar shifts of the 2-hydrogen to higher field as compared with the free base was observed in a number of authentic N-oxides.

Likewise, methyl 2-(2-pyridyl)propionate (**12**) gave three products when oxidized with *m*-chloroperbenzoic acid at room temperature. In this case, the major product was the N-oxide **15** but both the hydroxy compound **13** and its N-oxide **14** were also formed. On the other hand, the oxidation of 2-benzhydrylpyridine gave exclusively the N-oxide in high yield while methyl diphenylacetate was quite unreactive under our conditions. The oxidation of 2-(2-pyridyl)-1,3-indanedione (**16**) gave a 57% yield of the hydroxy compound **17**. Although at least three other compounds were present in the reaction mixture, we were not able to separate and identify them. The infrared and nmr spectra of this compound failed to distinguish between structure **17** and the isomeric N-oxide. The mass spectrum, however, was quite conclusive. (See Experimental Section.)

The loss of a C_2O_2 specie in the process *m/e* 211 → *m/e* 155 is rather unusual, but it is the only way the presence of a prominent metastable peak at *m*/e* 113.9 can be accommodated. In addition, the appearance of the ion *m/e* 76 as one of high relative abundance is also quite interesting. It probably represents benzyne which in the mass spectrum of indanetrione[7] is indeed the most abundant ion; hence its formation from structure **17** is not surprising.

Some simple kinetic measurements were carried out in order to obtain some information about the mechanism. The rates were measured by following the consumption of peracid iodometrically. In the case of **4** and **8**, the reaction was so fast that 5×10^{-4} *M* concentrations were necessary, which somewhat impaired the accuracy of the measurements. Nevertheless, good second-order rate constants were obtained for most reactions listed in Table I. In the case of the amide **8**, the activation enthalpy at 300°K was found to be $\Delta H^{\ddagger} = 12.5$ kcal and the activation entropy calculated as $\Delta S^{\ddagger} = -22.3$ cal deg^{-1}.

Discussion

Oxidation at the α carbon (α oxidation) of 2-picolinic derivatives with peracids apparently has no precedent in the literature. The well-known rearrangement of 2-picoline N-oxide and related derivatives to the corresponding α-hydroxy compounds in boiling acetic anhydride[6,8] comes to mind in this connection. It seemed quite unlikely, in view of the kinetic results recorded in Table I, that in the present reaction the N-oxides should be formed first and subsequently rearrange to the α-hydroxy isomers; the rate of oxidation of either the hydroxy amide **9** or 2-benzhydrylpyridine is much lower than that of compounds **4** and **8**. Nevertheless it was established that the N-oxides **11** and **15** were quite unreactive under our conditions.

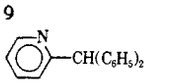
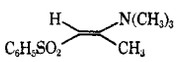
The results show that α oxidation takes place only with compounds having a nitrogen atom β to the reaction site; furthermore, an adjacent carbonyl function also appears to be a structural condition for reaction. The sequence depicted below accommodates these requirements (Scheme I). A very fast deuterium exchange at the α carbon of **4** took place in the presence of 1-deuterioacetic acid, thus demonstrating the presence of the equilibrium. The uv spectrum of the ester, however, did not provide any further evidence for its presence; the addition of acetic acid only caused a change in the fine structure and increased the intensity

(6) E. Ochiai, "Aromatic Amine Oxides," Elsevier Publishing Co., Amsterdam, 1967.

(7) R. F. C. Brown and R. K. Solly, *Aust. J. Chem.*, **19**, 1045 (1966).

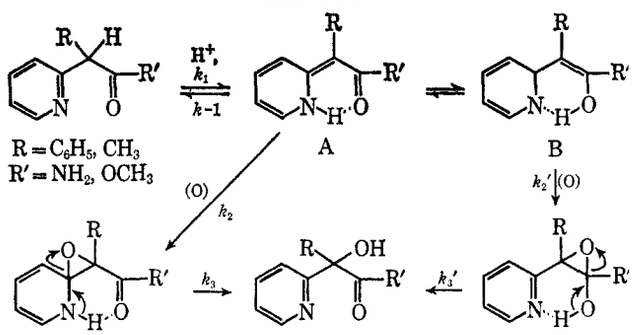
(8) R. Bodalski and A. R. Katritzky, *Tetrahedron Lett.*, 257 (1968), and references therein.

TABLE I
SECOND-ORDER RATES OF PERACID OXIDATIONS[a]

Compound	Peracid	Temp, °K	$k \times 10^2$ l. mol^{-1} sec^{-1}
4	MCPB[b]	296.4	50.6
4	PA[c]	296.4	2.6
8	MCPB	273.0	7.6
8	MCPB	296.5	53.2
8	MCPB	307.7	78.6
9	MCPB	296.1	0.43
	MCPB	295.8	7.1
	MCPB	273.0	1670

[a] In $CHCl_3$ as solvent. [b] *m*-Chloroperbenzoic acid. [c] Peracetic acid.

SCHEME I



of the absorption. This indicates that the equilibrium even in the presence of acid is shifted far to the left.

The second-order rate constants are in agreement with the scheme on the reasonable assumptions that $k_3 \gg k_2$ and that the above equilibrium is rapidly established. The observed rate constants are then a product of the actual rate constant k_2 and the equilibrium constant $K = k_1/k_{-1}$.[9] As far as information about the tautomerism A $\rightleftharpoons$ B is concerned, our data are inconclusive. Hence, any speculation as to which tautomer is actually being oxidized seems of little value to the present discussion; in either case the net result as depicted above would most likely be the same. The exocyclic double bond of A (and B) is electron rich and should react quickly with peracids. For comparison the rate of oxidation of an enamine was sought; 1-dimethylamino-2-methyl-1-propene reacted far too quickly even at 0° to be followed kinetically by conventional methods, but the phenylsulfonyl analog gave a fairly accurate rate constant. The rate (see Table I) is about 200 times faster than those observed for the pyridine derivatives; however, the actual rates of the latter would be comparable if K approximates 10^{-2} which is not an unreasonable value. Furthermore, the entropy of activation for the amide **8**, -22.3 cal deg^{-1}, compares very well with the values -21 to -25 cal deg^{-1} reported by Lynch and Pausacker[10] for the peracid oxidation of various olefins, indicating that the transition states of the two reactions are similar.

The fact that the ester **4** and the amide **8** react at about the same rate is reasonable on the basis of substituent effects;[11] certainly, the slightly higher rate of the amide is in the right direction. The influence of the substituent R on the rate of α oxidation can also be rationalized. Although no kinetic data are available for compound **12**, it is quite apparent from our results that a methyl group retards the rate as compared with a phenyl group,[12] contrary to what has been observed in epoxidation reactions;[13] clearly, the over-riding factor is the state of the equilibrium which certainly must be shifted considerably more to the right in the case of the phenyl-substituted ester **4**.

The formation of the dioxidized products **6**, **10**, and **14** is readily explained by further oxidation of the corresponding hydroxy compounds; as expected, the N-oxide **15** was completely unreactive toward peracid, thus eliminating that route.

Experimental Section[14]

Reagents.—The α-phenylpyridineacetic acid esters or amides were prepared according to known procedures.[4]

The oxidizing agents were either a 25% solution of peracetic acid in ethyl acetate made by Union Carbide Chemicals Division, South Charleston, W. Va., or *m*-chloroperbenzoic acid purchased from Research Organic Chemicals Co., Sun Valley, Calif.

Oxidation of Pyridine Derivatives with Peracids. General Procedure. A.—To a stirred solution or slurry of the pyridine derivative (100 mmol) in 100 ml of methylene chloride a 10% solution of *m*-chloroperbenzoic acid (100 mmol) in methylene chloride was added dropwise with stirring during 30 min. The reaction mixture was left at room temperature overnight. This was only a matter of convenience since the reactions were complete after about 4 hr reaction time. The absence of peracid was checked in the usual way. The precipitated *m*-chlorobenzoic acid was filtered and the filtrate washed with aqueous sodium bicarbonate, water and dried ($MgSO_4$). The solution was analyzed by tlc. The solvent was then evaporated and the product isolated and purified by conventional methods.

B.—To a stirred solution or slurry of the pyridine derivative (100 mmol) in 250 ml of ethyl acetate, peracetic acid (100 mmol) in ethyl acetate was added dropwise. The reaction mixture was allowed to stir at room temperature overnight. A test for unreacted peracid was performed. The ethyl acetate was removed on the rotary evaporator; the residue was taken up in chloroform or methylene chloride, washed with aqueous sodium bicarbonate and water, and dried ($MgSO_4$). The solution was analyzed by tlc and pure products were obtained as under A.

Methyl α-phenyl-3-pyridineacetate was prepared in 73% yield by leading dry hydrogen chloride into a methanolic solution of the corresponding amide:[4] bp 130° [bath temp (0.2 mm)];

(9) If the equilibrium between A and B is real, a more complicated picture will result, but the order of the reaction will not change.

(10) B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, 1525 (1955).

(11) C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, **2**, 323 (1964).

(12) It is assumed that any change in R will not substantially influence the rate of oxidation at nitrogen.

(13) W. R. Wragg, *Bull. Soc. Chim. Fr.*, 911 (1952).

(14) Melting points and boiling points are uncorrected. Infrared spectra were obtained with Beckman IR-5A spectrometer. The nmr spectra were measured with a Varian A-60 instrument. The chemical shifts are given in δ values. For thin layer chromatography Merck's plates precoated with 0.25 mm thickness of silica gel F-254 were used.

$n^{20}D$ 1.5719; nmr (CCl_4) s 3.59 (CH_3), s 5.09 (CH), m 6.8–7.8 (Ar).

Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16. Found: C, 73.64; H, 6.02; N, 6.45.

α-Phenyl-3-pyridineacetic acid was prepared in 90% yield by saponification of the above ester with aqueous methanolic sodium hydroxide, mp 148° dec from ethanol.

Anal. Calcd for $C_{13}H_{11}NO_2$: C, 73.22; H, 5.20; N, 6.57. Found: C, 72.91; H, 5.23; N, 6.91.

α-Phenyl-3-pyridineacetic Acid N-Oxide (1).—The acid was insoluble in ethyl acetate, and the oxidation was performed in tetrahydrofuran with peracetic acid. The N-oxide was obtained in 79% yield: mp 158° dec from ethanol; ν_{max} (KBr) 1235 cm^{-1} (NO); nmr (DMSO) 5.27 (CH), 7.4–8.4 (Ar).

Anal. Calcd for $C_{13}H_{11}NO_3$: C, 68.11; H, 4.84; N, 6.11. Found: C, 68.79; H, 4.89; N, 6.20.

Methyl α-phenyl-4-pyridineacetate N-oxide (2) was obtained as a liquid in 95% crude yield: picrate mp 127–129° from ethanol (lit.[5] mp 133°); ν_{max} 1230 cm^{-1} (NO); nmr ($CDCl_3$) s 4.27 (CH_3), s 5.10 (CH), m 7.3–8.5 (Ar).

α-Phenyl-4-pyridineacetic acid N-oxide (3) was obtained in 85% yield by saponifying 2 in the usual way with 10% sodium hydroxide, mp 95° dec (lit.[5] mp 98–99° dec).

Methyl α-phenyl-2-pyridineglycolate (5) was obtained in 63% yield from the ester 4, mp 66–67.5° from ethanol–water, 1:1; ν_{max} (KBr) 3400 cm^{-1} (OH); nmr ($CDCl_3$) s 3.80 (CH_3), m 7.2–7.8 (Ar), m 8.55 (Ar, –CH=N–).

Anal. Calcd for $C_{14}H_{13}NO_3$: C, 69.12; H, 5.39; N, 5.76. Found: C, 68.80; H, 5.22; N, 5.90.

Hydrolysis of 5 with sodium hydroxide in methanol–water gave a 72% yield of **phenyl-2-pyridylcarbinol** (7), mp 76–78° (lit.[15] mp 82°).

Methyl α-phenyl-2-pyridineglycolate N-oxide (6) was obtained from 4 together with 5, and separated from the latter by chromatography on silica gel. It was obtained in 74% yield by treating 4 with 3 *M* excess of peracid: mp 137° from ethyl acetate; ν_{max} (KBr) 3350 (OH) 1230 cm^{-1} (NO); nmr ($CDCl_3$) s 3.82 (CH_3), m 6.7–7.9 (Ar), m 8.30 (Ar, –CH=N—O).

Anal. Calcd for $C_{14}H_{13}NO_4$: C, 64.86; H, 5.05; N, 5.40. Found: C, 64.67; H, 5.03; N, 5.28.

α-Phenyl-2-pyridineglycolamide (9) was prepared from the amide 8 in 57% yield: mp 131° from ethyl acetate; ν_{max} (KBr) 3450 cm^{-1} (OH); nmr (DMSO) m 7.2–7.9 (Ar), m 8.60 (Ar, CH=N–).

Anal. Calcd for $C_{13}H_{12}N_2O_2$: C, 68.41; H, 5.30; N, 12.27. Found: C, 68.25; H, 5.30; N, 12.44.

α-Phenyl-2-pyridineglycolamide N-oxide (10) was obtained together with 11 in 29% yield from the same reaction producing compound 9. A pure sample was obtained after several recrystallizations fom ethyl acetate: mp 205°; ν_{max} (KBr) 3400 (OH), 1230 cm^{-1} (NO); nmr (DMSO) m 7.3–7.7 (Ar), m 8.45 (Ar, CH=NO).

Anal. Calcd for $C_{13}H_{12}N_2O_3$: C, 63.93; H, 4.95; N, 11.47. Found: C, 63.47; H, 5.15; N, 11.52.

This compound is the sole product when 8 is oxidized with a 3 *M* excess of peracid.

α-Phenyl-2-pyridineacetamide N-oxide (11) was obtained together with 10 in 29% yield. A pure sample was obtained after recrystallization from benzene: mp 152°; ν_{max} (KBr) 1240 cm^{-1} (NO); nmr (DMSO) s 5.55 (CH), m 7.0–7.8 (Ar), m 8.35 (Ar, –CH=N—O).

Anal. Calcd for $C_{13}H_{12}N_2O_2$: C, 68.41; H, 5.30; N, 12.27. Found: C, 68.15; H, 5.09; N, 12.01.

Methyl 2-(2-Pyridyl)propionate (12).—To a slurry of 4.3 g of sodium hydride (56.5% in mineral oil) in 50 ml of dry tetrahydrofuran was added with stirring 15.1 g (0.1 mol) of methyl 2-pyridylacetate; 30 min after the addition was complete the reaction mixture became homogeneous. This solution was added dropwise to a water-cooled solution of 42.6 g (0.3 mol) of methyl iodide in 50 ml of tetrahydrofuran. The reaction mixture was left overnight and then workedup in the usual way. A second product was present. Distillation gave 9.7 g (59%) of a liquid; bp 62° (0.7 mm), $n^{22}D$ 1.5020. Glpc showed that 10% of a second compound was present. Fractionation gave a pure sample of 12.

Anal. Calcd for $C_9H_{11}NO_2$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.42; H, 6.76; N, 8.64.

Although it was not isolated, the nmr spectrum showed that the impurity must be methyl 2-methyl-2-(2-pyridyl)propionate.

Methyl 2-(2-pyridyl)lactate (13) was obtained together with compounds 14 and 15 by oxidation of 12 in a combined yield of 90%. By chromatography on silica gel 21% of the mixture was separated as a liquid (13) which was not distilled: ν_{max} (liq) 3400 cm^{-1} (OH); nmr (CCl_4) s 1.72 (CH_3), s 3.62 (OCH_3), m 7.1–7.9 (Ar), m 8.52 (Ar, –CH=N–).

Methyl 2-(2-pyridyl)lactate N-oxide (14) was separated from compounds 13 and 15 by chromatography on silica gel and recrystallized from ethyl acetate, mp 143–147°.

Anal. Calcd for $C_9H_{11}NO_4$: C, 54.82; H, 5.62; N, 7.10. Found: C, 55.45; H, 5.86; N, 7.06.

This compound represented about 10% of the mixture.

Methyl 2-(2-pyridyl)propionate N-oxide (15) was separated from compounds 13 and 14 by chromatography on silica gel and recrystallized from carbon tetrachloride: mp 70–73°; nmr (CCl_4) d 1.50 (CH_3), s 3.62 (OCH_3), m 7.1–7.5 (Ar), 8.12 (Ar, –CH=N—O).

Anal. Calcd for $C_9H_{11}NO_3$: C, 59.66; H, 6.12; N, 7.73. Found: C, 59.54; H, 6.19; N, 7.80.

2-Hydroxy-2(2-pyridyl)-1,3-indanedione (17) was obtained in 54% yield by the oxidation of 2(2-pyridyl)-1,3-indanedione[16] with *m*-chloroperbenzoic acid: mp 212° from ethanol; λ_{max} (methanol) 233 (17,000), 267 (7400) 342.5 nm (ε 17,500); for mass spectrum see Table II.

Anal. Calcd for $C_{14}H_9NO_3$: C, 70.29; H, 3.79: N, 5.87 Found: C, 70.46; H, 3.96; N, 5.71.

TABLE II

MASS SPECTRUM

m/e	Rel abundance	*m/e*	Rel abundance
239	90	105	38
223	7	104	14
211	31	79	36
182	31	78	38
155	100	77	52
154	55	76	45
133	4	52	40
127	12	51	43
106	13	50	38

2-Benzhydrylpyridine N-oxide was obtained in 84% yield by oxidation of the free base with peracid, mp 159° from ethanol; ν_{max} (KBr) 1250 cm^{-1} (N–O).

Anal. Calcd for $C_{18}H_{15}NO$: C, 82.73; H, 5.79; N, 5.36. Found: C, 82.43; H, 5.73; N, 5.49.

Registry No.—1, 21883-21-6; 2, 21883-22-7; 5, 21883-23-8; 6, 21883-24-9; 9, 21883-25-0; 10, 21883-26-1; 11, 21904-44-9; 12, 21883-27-2; 13, 21883-28-3; 14, 21883-29-4; 15, 21883-30-7; 17, 7421-75-2; methyl α-phenyl-3-pyridineacetate, 21883-32-9; α-phenyl-3-pyridineacetate acid, 21883-33-0; 2-benzhydrylpyridine N-oxide, 21883-34-1.

(15) A. E. Tschitschibabin, *Ber.*, **37**, 1371 (1904).

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