Base-Catalyzed Redox Reactions of α-Hydroxyalkylazaaromatic *N*-Oxides (1,2)

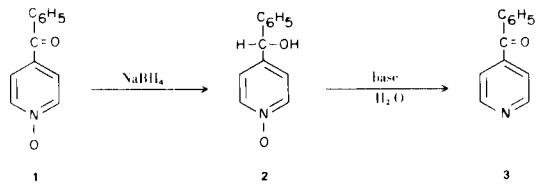
Chester W. Muth, Jesse C. Patton (3a), Bhabatosh Bhattacharya (3b), David L. Giberson (3c), and Christopher A. Ferguson (3d)

Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506

Received August 14, 1972

The (α-hydroxybenzyl)pyridine 1-oxides on heating with aqueous sodium hydroxide yielded the corresponding benzoylpyridines in redox reactions. When the phenyl groups of the foregoing compounds was replaced by hydrogen or methyl the redox reactions occurred less readily. A kinetic isotope effect of 3 was found for 4-(α-deuterio-α-hydroxybenzyl)pyridine 1-oxide on reaction with sodium hydroxide. The removal of the α-deuterio group is non-reversible. A mechanism consistent with these observations is given. 6-Acetoxyphenanthridine 5-oxide yielded with concentrated hydrochloric acid a redox product, 6-formylphenanthridine hydrochloride, whereas under the same conditions neither (α-hydroxybenzyl)pyridine 1-oxides nor 2-hydroxymethylquinoline 1-oxide yielded a redox product.

A synthesis of 4-(α-hydroxybenzyl)pyridine 1-oxide (**2**) was desired for a study to determine whether it is an intermediate in the reaction of 4-benzoylpyridine 1-oxide (**1**) with ethanolic sodium hydroxide to yield 4-(α-hydroxybenzyl)pyridine (4). The treatment of 4-benzoylpyridine 1-oxide with sodium borohydride and hydrolysis of the reaction mixture without adding acid yielded 4-benzoylpyridine (**3**) (72%) and a small amount of the desired 4-(α-hydroxybenzyl)pyridine 1-oxide (**2**). Subsequently we found that if the reaction mixture from the treatment of 4-benzoylpyridine 1-oxide (**1**) with sodium borohydride is acidified before hydrolysis the sole product is 4-(α-hydroxybenzyl)pyridine 1-oxide (**2**). From this it was concluded that 4-benzoylpyridine 1-oxide (**1**) reacted with sodium borohydride to yield 4-(α-hydroxybenzyl)pyridine 1-oxide (**2**) which is stable under acidic conditions but which under basic conditions took part in a redox reaction. This type reaction has been reported recently for the pyridine 1-oxide (5), quinoxalinone 1-oxide (6,7), and benzotriazine 1-oxide series (8).



1 2 3

2-Benzoylpyridine 1-oxide likewise yielded 2-benzoylpyridine (redox product) on reaction with sodium borohydride when no acid was added during the hydrolysis of the reaction mixture, whereas 3-benzoylpyridine 1-oxide under the same conditions yielded 3-(α-hydroxybenzyl)-pyridine 1-oxide.

In an effort to learn more about the nature of these base-promoted redox reactions, 2-, 3-, and 4-(α-hydroxybenzyl)pyridine 1-oxides (9) were reacted with aqueous sodium hydroxide. The results are shown in Table I. These data show that the 3-isomer is the least likely to undergo the redox reaction and that the redox reaction is base-catalyzed (last entry).

Rate studies were conducted on 0.5 *M* 4-(α-hydroxybenzyl)pyridine 1-oxide and on 0.5 *M* 4-(α-deuterio-α-hydroxybenzyl)pyridine 1-oxide in the presence of 0.38 *M* sodium deuterioxide in 13:7 deuterium oxide-ethanol solutions. The product from both reactions was 4-benzoylpyridine. The pseudo first-order rate constants for the protio and deuterio compounds were 6×10^{-4} sec^{-1} and 2×10^{-4} sec^{-1}, respectively, for a kinetic isotope effect of 3. The rates were monitored by following the disappearance of the nmr signal for the 2- and 6-hydrogens (τ 1.6-1.7) of 4-(α-hydroxybenzyl)pyridine 1-oxide (**2**). Since these hydrogens may have to a certain extent undergone exchange with deuterium (10) and since the α-deuterio compound reacted more slowly, the kinetic isotope effect may be greater than 3. The removal of the deuteron from the carbinol carbon as determined by nmr measurements is irreversible. Consequently the removal of a proton or deuteron from the carbinol carbon is not only the rate-determining step but it is also a nonreversible step in this redox reaction.

In an effort to learn more about the scope of the redox

TABLE I

Reactions of (α-Hydroxybenzyl)pyridine 1-Oxides with Aqueous Sodium Hydroxide (a)

Isomer	NaOH Conc.	NaOH/*N*-oxide Molar Ratio	Reaction Time, Hr.	% Yield Benzoylpyridine (m.p.°)	
2	1 *N*	4	14	99	(44-46)
3	1 *N*	5	16	45	(41-42)
4	1 *N*	2.5	10	99	(72)
4	0.5 *N*	1	0.25	98	(65-66)
4	0.05 *N*	0.1	72	99	(72-74)

(a) Steam bath temperature except for third entry which was at 85°.

TABLE II

Redox Reactions of (α-Hydroxyalkyl)aromatic *N*-Oxides with Equimolar Amounts of Aqueous Sodium Hydroxide and Phenylhydrazine

	NaOH Norm.	Reaction Time, Hr.	Reaction Temp.°	% Yield Phenylhydrazone Redox Product and m.p.°	
(a) 2-Hydroxymethylpyridine 1-oxide	- - -	3	80	18	(174-176)
(a) 3-Hydroxymethylpyridine 1-oxide	- - -	20	80	No reaction	
(a) 4-Hydroxymethylpyridine 1-oxide	- - -	4	80	70	(175-176)
(b) 4-Hydroxymethylpyridine 1-oxide	- - -	26	100	52	(51-53)
2-(α-Hydroxyethyl)pyridine 1-oxide	0.5	69	100	15	(149-152)
(a) 2-(α-Hydroxyethyl)pyridine 1-oxide	- - -	3	80	19	(147-151)
(b) 3-(α-Hydroxyethyl)pyridine 1-oxide	0.7	20	100	No reaction	
4-(α-Hydroxyethyl)pyridine 1-oxide	1	7	100	54	(148-150)
(b) 4-(α-Hydroxyethyl)pyridine 1-oxide	1	7	100	14 (d)	
(a) 2-Hydroxymethylquinoline 1-oxide	- - -	0.3	80	77	(205-206)
2-Hydroxymethylquinoline 1-oxide	0.7	0.3	100	100	(210-212)
8-Hydroxy-5,6,7,8-tetrahydroquinoline 1-oxide	1	18	100	62	(182-184)
(b) 8-Hydroxy-5,6,7,8-tetrahydroquinoline 1-oxide	1	21	100	No reaction	

(a) W. S. Chilton and A. K. Butler, ref. 5. (b) No phenylhydrazine used. (c) % Yield of 4-hydroxymethylpyridine (Cannizzaro product of 4-formylpyridine). (d) % Yield of 4-acetylpyridine based on nmr analysis.

reaction the carbinol substituent was changed from phenyl to hydrogen or methyl. In this connection the results of Chilton and Butler (5) were supplemented. The results are summarized in Table II.

TABLE III

Preparation of α-(Hydroxyalkyl)pyridine or quinoline 1-Oxides

Compound	Method of Prep.	M.p., °C	% Yield	Analysis Calculated (Molecular Formula)	Found (a)
2-(α-Hydroxybenzyl)-pyridine 1-oxide	A	166-167 (b)	84	C, 71.70; H, 5.51; N, 6.96 ($C_{12}H_{11}NO_2$)	C, 71.83; H, 5.64; N, 6.90
3-(α-Hydroxybenzyl)-pyridine 1-oxide	A	117-118 (c)	78	C, 71.70; H, 5.51; N, 6.96 ($C_{12}H_{11}NO_2$)	C, 71.80; H, 5.56; N, 6.90
4-(α-Hydroxybenzyl)-pyridine 1-oxide	A	177-180 (d)	83	C, 71.70; H, 5.51; N, 6.96 ($C_{12}H_{11}NO_2$)	C, 71.74; H, 5.47; N, 6.87
4-(α-Deuterio-α-hydroxy-benzyl)pyridine 1-oxide	A	173-178 (e)	77	9.10 atom % excess deuterium ($C_{12}H_{10}DNO_2$)	8.94 atom % excess deuterium (f)
2-(α-Hydroxyethyl)-pyridine 1-oxide	B	100-101 (g)	57		
3-(α-Hydroxyethyl)-pyridine 1-oxide	A	110-112 (h)	38	C, 60.42; H, 6.52; N, 10.07 ($C_7H_9NO_2$)	C, 60.56; H, 6.22; N, 9.95
4-(α-Hydroxyethyl)-pyridine 1-oxide	A	69-70 (i)	29	C, 60.42; H, 6.52; N, 10.07 ($C_7H_9NO_2$)	C, 60.65; H, 6.68; N, 9.90
2-Hydroxymethylquinoline 1-oxide	B	136-138 (j)	36	C, 68.56; H, 5.18; N, 7.99 ($C_{10}H_9NO_2$)	C, 68.69; H, 5.03; N, 7.87
8-Hydroxy-5,6,7,8-tetra-hydroquinoline 1-oxide	B	120-125 (k)	97		

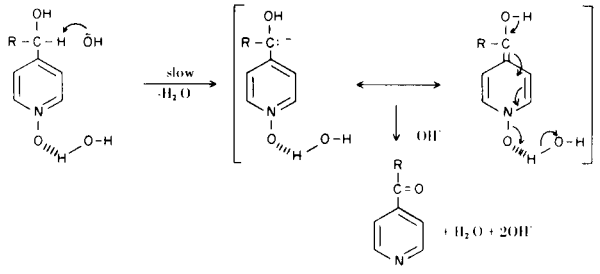
(a) By Galbraith Laboratories, Knoxville, Tenn. unless otherwise indicated. (b) From ethanol-ligroin; ir (potassium bromide) 3170 (OH), 1210 cm^{-1} (N-O). (c) From ethanol; ir (potassium bromide) 3400 (broad OH) and 1240 cm^{-1} (N-O). (d) From ethanol; ir (potassium bromide) 1220 cm^{-1} (N-O); nmr (DMSO) τ 2.1 (d, 2, 2,6-pyridine 1-oxide), 2.9 (m, 7, aromatic), 4.0 (d, 1, O*H*), and 4.4 (d, 1, C*H*OH). (e) After two crystallizations from absolute ethanol, m.p. 178-179°, no appreciable m.p. depression with nondeuterated compound; nmr (DMSO) no signal for C*H*OH. (f) Deuterium analysis by Jesef Nameth, 363 W. Washington St., Urbana, Ill. 61801. (g) From benzene-ligroin; V. Boekelheide and W. J. Linn, *J. Am. Chem. Soc.*, **76**, 1290 (1954), m.p. 97-99°; ir (potassium bromide) 3200 (OH) and 1210 cm^{-1} (N-O); nmr (deuteriochloroform) τ 1.8 (m, 1, aromatic), 2.8 (m, 3, aromatic), 4.1 (d, 1, O*H*), 4.8 (q, 1, CH_3CH), 8.4 (d, 3, CH_3). Modified Method B: 2-acetylpyridine was treated with sodium borohydride and the resulting alcohol was reacted with acetyl chloride and pyridine in benzene to yield the acetate. (h) From benzene-chloroform; ir (potassium bromide) 3450 (OH) and 1250 cm^{-1} (N-O); nmr (deuteriochloroform) τ 1.7 (m, 2, aromatic), 2.5 (m, 2, aromatic), 4.3 (broad s, 1, OH), 5.0 (q, 1, CH_3CH), 8.5 (d, 3, CH_3). (i) Triturated with ether; ir (potassium bromide) 3400 (OH) and 1220 cm^{-1} (N-O); nmr (deuteriochloroform) τ 1.8-2.0 (d, 2, aromatic), 2.6-2.8 (d, 2, aromatic), 4.3 (d, 1, O*H*), 4.9-5.3 (q, 1, CH_3CH), 8.4-8.6 (d, 3, CH_3). (j) From benzene, E. Ochiai, *et al.*, *Yakugaku Zasshi*, **80**, 339 (1960); *Chem. Abstr.*, **54**, 18525 (1960), m.p. 131°. (k) D. B. Weser, M. S. Thesis, West Virginia University, Morgantown, W. Va., 1966, p. 35, m.p. 120-125°. We are grateful to Professor D. W. H. MacDowell for graciously supplying a sample of 8-acetoxy-5,6,7,8-tetrahydroquinoline.

Three aspects of the data will be emphasized. First, if the phenyl group attached to the carbinol carbon is replaced by either hydrogen or methyl the yield of the redox product is reduced. This is in agreement with the expected greater stabilizing effect of the phenyl group on the rate-determining step in comparison to the influence of hydrogen or methyl on the same step. Secondly, the fact that 2-hydroxymethylquinoline 1-oxide reacts the most rapidly in the redox reaction of the compounds listed in Table II may be explained by the presence of an extra benzo group which can be expected to stabilize the transition state leading to the removal of a proton in the rate-determining step. Third, the redox reaction of 8-hydroxy-5,6,7,8-tetrahydroquinoline 1-oxide occurred in the presence of phenylhydrazine but did not occur in the absence of phenylhydrazine (11). No satisfactory explanation is available for this observation.

As a sequel to the foregoing observation, 4-(α-hydroxyethyl)pyridine 1-oxide was treated with an equimolar amount of sodium hydroxide at 100° in the absence and in the presence of phenylhydrazine to yield 4-acetylpyridine phenylhydrazone (54%) and 4-acetylpyridine (14%), respectively. The low yield of 4-acetylpyridine may be due to its instability in the presence of base. In a separate experiment 4-acetylpyridine was found to undergo reaction with sodium hydroxide at 100°.

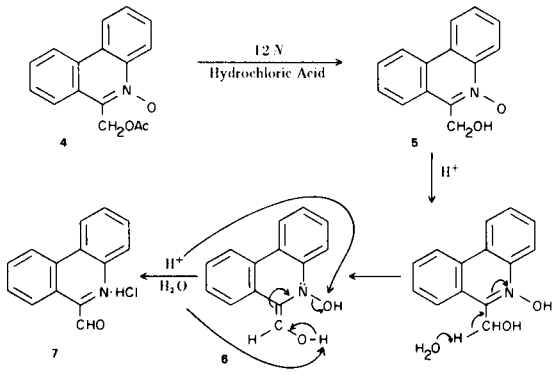
When reactions of 4-(α-deuterio-α-hydroxyethyl)pyridine 1-oxide with sodium hydroxide both with and without phenylhydrazine were interrupted there was no evidence of deuterio-protio exchange at the carbinol carbon. This parallels the results obtained with 4-(α-hydroxybenzyl)pyridine 1-oxide.

A mechanism consistent with our results is:



This mechanism is consistent with the lower reactivity of the 3-(α-hydroxyalkyl)pyridine 1-oxides in the redox reaction. In the latter case the ring nitrogen cannot help stabilize the anion by accepting a pair of electrons.

Acid-promoted redox reactions were not observed with α-hydroxyalkylpyridine *N*-oxides whereas we did observe that 6-acetoxymethylphenanthridine 5-oxide (**4**) reacted with concentrated hydrochloric acid to yield 6-formylphenanthridine hydrochloride (**7**), presumably by a redox reaction. Acid-promoted redox reactions have also been observed in the quinoxalinone 1-oxide (6) and benzotriazine 1-oxide (8) series. Apparently the redox reaction is more likely to occur under basic conditions but it can also be expected to occur under acidic conditions for those compounds which can readily form a *N*-hydroxy anhydro base such as **6**.



EXPERIMENTAL

All temperatures are uncorrected. Infrared spectra were recorded on a Beckman IR-8 or a Perkin-Elmer IR-137 spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Varian HA-60 or T-60 spectrometer with TMS or DSS as the internal standard.

All benzoylpyridines, acetylpyridines, and hydroxymethylpyridine 1-oxides were obtained from commercial sources and were recrystallized if necessary.

(α-Hydroxyalkyl)pyridine 1-Oxides.

Method A.

A typical example of this method, the preparation of 2-(α-hydroxybenzyl)pyridine 1-oxide, will be described. The results for this reaction and others performed by Method A are summarized in Table III.

2-Benzoylpyridine 1-oxide (4) (2.30 g., 0.012 mole), sodium borohydride (0.2 g., 0.067 mole), and 20 ml. of absolute ethanol were stirred at room temperature for 5 hours (for reductions of some compounds the reaction time was as little as ½ hour). After acidifying the solution with 6 *N* hydrochloric acid the volume was decreased *in vacuo*, neutralized with solid sodium carbonate, and extracted with chloroform. The chloroform was removed *in vacuo* and the residue was recrystallized from ethanol-ligroin yielding 2.07 g. (84%) of 2-(α-hydroxybenzyl)pyridine 1-oxide as colorless crystals, m.p. 166-167°.

Method B.

The preparation of 6-acetoxymethylphenanthridine 5-oxide (**4**) is typical of the first steps of Method B. The results of the hydrolysis of the foregoing compound in concentrated hydrochloric acid are atypical in that presumably 6-hydroxymethylphenanthridine 5-oxide (**5**) formed and subsequently reacted to yield 6-formylphenanthridine hydrochloride (**7**). The results for the hydrolysis of 2-acetoxymethylquinoline 1-oxide and 8-acetoxy-5,6,7,8-tetrahydroquinoline 1-oxide with 6 *N* hydrochloric acid after 9 and 6 hours, respectively, at 100° are summarized in Table III.

6-Methylphenanthridine 5-Oxide.

Forty percent peracetic acid (80.0 g., 1.05 moles) was dropped with stirring into 55.0 g. (0.285 mole) of 6-methylphenanthridine (12) dissolved in chloroform at such a rate that the temperature did not rise above 40°. The mixture was heated with stirring at 40-45° for 24 hours. The mixture was worked up in the usual way (4) to yield after recrystallization from 80% ethanol 53.0 g. (81%) of the monohydrate of the title compound: small light brown crystals; m.p. 110-112°, after 2 hours at 40-50°, m.p. 128-130° [lit. (13), m.p. 127-128.5°].

6-Acetoxymethylphenanthridine.

Five g. (0.0222 mole) of 6-methylphenanthridine 5-oxide monohydrate was stirred with 40 g. (0.39 mole) of acetic anhydride at room temperature for 4 hours. The mixture was filtered and the filtrate was concentrated under reduced pressure. The residue was stirred with water and made basic with sodium bicarbonate solution. The liberated oil was extracted with ether and the ethereal solution was washed with saturated sodium chloride solution and dried (sodium sulfate). The ethereal solution was concentrated and the residue was distilled to give a viscous yellow oil, b.p. 200-202°/0.5 mm. The distillate was crystallized from petroleum ether (60-80°) as 4.0 g. (65%) of small yellow crystals: m.p. 81-82°; ir (potassium bromide) 1730 (ester C=O), 1250 cm^{-1} (N-O); nmr (deuteriochloroform) τ 1.5-2.7 (m, 8, aromatic), 4.4 (s, 2, CH_2), 7.9 (s, 3, CH_3).

Anal. Calcd. for $C_{16}H_{13}NO_2$: C, 76.49; H, 5.18; N, 5.58; O, 12.75. Found: C, 76.37; H, 5.31; N, 5.31; O, 12.59.

6-Acetoxymethylphenanthridine 5-Oxide (**4**).

This was prepared as was 6-methylphenanthridine 5-oxide. The yield of light yellow micro crystals from aqueous ethanol was 60%: m.p. 149-150°; ir (potassium bromide) 1730 (ester C=O), 1300 cm^{-1} (N-O); nmr τ 1.0-2.5 (m, 8, aromatic), 4.0 (s, 2, CH_2), 7.9 (s, 3, CH_3).

Anal. Calcd. for $C_{16}H_{13}NO_3$: C, 71.91; H, 4.87. Found: C, 71.79; H, 5.03.

Reactions of (α-Hydroxybenzyl)pyridine 1-Oxides with Aqueous Sodium Hydroxide.

The reaction of 2-(α-hydroxybenzyl)pyridine 1-oxide with aqueous sodium hydroxide is typical of the other reactions summarized in Table I. 2-(α-Hydroxybenzyl)pyridine 1-oxide (1.45 g., 0.0073 mole) and 30 ml. of 1.0 *N* sodium hydroxide (0.030 mole) were stirred at 100° for 14 hours. An oil immediately separated from the reaction mixture when its temperature reached 100°. The reaction mixture was extracted with two 100-ml. portions of ether. The combined ether extract was dried (magnesium sulfate) and evaporated to give 1.30 g. (98%) of 2-benzoylpyridine: picrate, m.p. 127-129° [lit. (14) m.p. 128-129°]; ir (neat) was identical to that of authentic 2-benzoylpyridine.

Reactions of α-Hydroxyalkylpyridine 1-Oxides with Aqueous Sodium Hydroxide and Phenylhydrazine.

The reaction of 4-(α-hydroxyethyl)pyridine 1-oxide with equimolar amounts of aqueous sodium hydroxide and phenylhydrazine is typical of similar reactions summarized in Table II. 4-(α-Hydroxyethyl)pyridine 1-oxide (0.76 g., 0.0055 mole), 10 ml. of water, 0.23 g. (0.0057 mole) of sodium hydroxide, and 0.62 g. (0.0057 mole) of phenylhydrazine were stirred in a flask on a steam bath for 7 hours, cooled, and filtered to remove a yellow precipitate. Recrystallization of the precipitate from ethanol-water gave 0.58 g. (54%) of 4-acetylpyridine phenylhydrazone as yellow needles, m.p. 148-150°. A mixed m.p. with authentic 4-acetylpyridine phenylhydrazone gave no melting point depression.

In another experiment, 4-(α-hydroxyethyl)pyridine 1-oxide and aqueous sodium hydroxide were reacted under conditions identical to those used in the preceding experiment except no phenylhydrazine was employed. The percent yield of redox product, 4-acetylpyridine, was 14% based on nmr data.

Reaction of 4-(Hydroxymethyl)pyridine 1-Oxide with Aqueous Sodium Hydroxide.

4-Hydroxymethylpyridine 1-oxide (2.00 g., 0.016 mole), 0.80 g. (0.02 mole) of sodium hydroxide, and 20 ml. of water were stirred at 100° for 24 hours, cooled, and extracted with three 40-ml. portions of chloroform followed by extraction with two 60-ml. portions of 1-butanol. Removal of chloroform and 1-butanol from these extracts gave 0.46 g. (52%) of 4-hydroxymethylpyridine as colorless crystals, m.p. 51-53° [lit. (15) m.p. 52°]; picrate m.p. 165-167° [lit. (15) m.p. 165-166°]. This product was assumed to by formed by a Cannizzaro reaction from 4-formylpyridine which is the internal redox product of 4-hydroxymethoxymethylpyridine 1-oxide.

6-Formylphenanthridine Hydrochloride (**7**) from 6-Acetoxymethylphenanthridine 5-Oxide (**4**) and Concentrated Hydrochloric Acid.

6-Acetoxymethylphenanthridine 5-oxide (**4**) (1.5 g., 5.6 mmoles) was heated under reflux with 15 ml. of concentrated hydrochloric acid for 4 hours. The mixture was filtered while hot (charcoal) and the filtrate on cooling gave 0.81 g. of **7** which was recrystallized from absolute ethanol-ether as light yellow flakes which after drying over phosphorous pentoxide at 54°/2-3 mm for 8 hours melted at 280-282°. The product gave a 2,4-dinitrophenylhydrazone instantaneously. The nmr spectrum of the hydrochloride is superimposable on the nmr spectrum of authentic 6-formylphenanthridine hydrochloride. The product when treated with sodium bicarbonate solution yielded 6-formylphenanthridine, m.p. 138-139° [lit. (16) m.p. 138-139°], and a mixed m.p. with authentic 6-formylphenanthridine showed no depression.

Kinetic Studies of 4-(α-Protio- and α-Deuterio-α-hydroxybenzyl)-pyridine 1-Oxides with Sodium Hydroxide.

The *N*-oxide (0.050 g.) was dissolved in a solution of 0.5 *N* sodium deuterioxide in deuterium oxide and 0.15 ml. of absolute ethanol. After the sample was in position in a Varian HA-60 nmr spectrometer for 4-8 minutes, the first integration was made at τ 1.6-1.7. Additional integrations were taken every 6-8 minutes for the α-protio compound and every 8-15 minutes for the α-deuterio compound through two half-lives. The temperature was measured before and after each run by a thermocouple with one junction in ice and the other in ethylene glycol in the nmr probe. For six determinations with the α-protio compound the temperature varied 1° or less per determination and between 72.3 and 75.0° in different determinations. Four determinations were made for the α-deuterio compound under similar conditions. The log of the integrations were plotted versus time. From the slopes of the graphs the average pseudo first-order rate constants for the α-protio and α-deuterio compounds were 6×10^{-4} sec^{-1} and 2×10^{-4} sec^{-1}, respectively.

REFERENCES

(1) Supported in part by the West Virginia University Senate Committee on Research Grants (JCP) and by the 1971 National Science Foundation Undergraduate Research Participation Program (DLG).

(2) Presented in part before the First Central Regional Meeting of the ACS, Akron, Ohio, May, 1968, in part before the Second International Congress of Heterocyclic Chemistry, Montpellier, France, July, 1969, and in part before the West Virginia Academy of Science, Morgantown, West Virginia, April, 1971.

(3a) Taken from Ph.D. dissertation (1972); (b) Taken from M.S. thesis (1970); (c) NSF Undergraduate Research Participant, summer, 1971; (d) Senior research (1970-1971).

(4) C. W. Muth, R. S. Darlak, and J. C. Patton, *J. Heterocyclic Chem.*, 1003 (1972).

(5) W. S. Chilton and A. K. Butler, *J. Org. Chem.*, 32, 1270 (1967).

(6) M. J. Haddadin and C. H. Issorides, *Tetrahedron Letters*, 44, 4609 (1968).

(7) A. S. Elina, L. Tsyrul'nikova and G. Syrova, *Khim. Geterotskil. Soedin*, 1, 149 (1969).

(8) G. Tennant, *J. Chem. Soc., (C)*, 2658 (1967).

(9) The (α-hydroxyalkyl)aromatic *N*-oxides are of interest because of their antibacterial activity, J. Francis, J. K. Landquist, A. A. Levi, and J. M. Thorp, *Biochem. J.*, 63, 455 (1956).

(10) J. A. Zoltewicsz and H. S. Helmick, *J. Am. Chem. Soc.*, 92, 7547 (1970).

(11) Chilton and Butler (ref. 5) show that phenylhydrazine is neither an oxidizing or reducing agent in the redox reactions they studied.

(12) G. T. Morgan and L. P. Walls, *J. Chem. Soc.*, 2447 (1931).

(13) T. M. Mishina and L. S. Efros, *Zh. Obshch. Khim.*, 32, 2217 (1962); *Chem. Abstr.*, 58, 9023 (1963).

(14) F. Anderson, C. Duca, and J. Scudi, *J. Am. Chem. Soc.*, 73, 4967 (1951).

(15) Ravenna, *Farmaco (Pavia), Ed. Sci.*, 14, 483 (1959); *Chem. Abstr.*, 55, 9929 (1961).

(16) E. Ritchie, *J. Proc. Roy. Soc., N. Wales*, 78, 134 (1945); *Chem. Abstr.*, 40, 879 (1946).