Hydroxide-promoted Redox Reactions in Water of α-Phenyl-4-nitrobenzenemethanol, α-(*p*-Nitrophenyl)-4-pyridinemethanol, and α-(*p*-Nitrophenyl)-4-Pyridinemethanol *N*-Oxide
Steric Inhibition of Resonance

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α-Phenyl-4-nitrobenzenemethanol (**3**) reacted with 1 *M* sodium hydroxide to yield 4,4'-dibenzoylazoybenzene (**5**) (51%), 4-hydroxy-4'-benzoylazobenzene (**6**) and benzoic acid (12% each), and smaller amounts of 4-aminobenzophenone and 4-nitrobenzophenone. Both α-phenyl-2-nitrobenzenemethanol (**9**) and 3,5-dimethyl-4-nitrobenzenemethanol (**10a**) did not react with 1 *M* sodium hydroxide, presumably due to steric hindrance. α-(*p*-Nitrophenyl)-4-pyridinemethanol (**14**) and its *N*-oxide **11** with 1 *M* sodium hydroxide yielded 4,4'-diaroylazoxybenzenes **15a** and **12a**, respectively, 4,4'-diaroylazobenzenes **15b** and **12b**, respectively, as well as 4-hydroxy-4'-aroylazobenzenes **16** and **13**, respectively. The relative reaction rates were **11** > **14** > **3**. Studies with **11** showed that the nitro group is involved in the redox reaction in preference to the *N*-oxide group.

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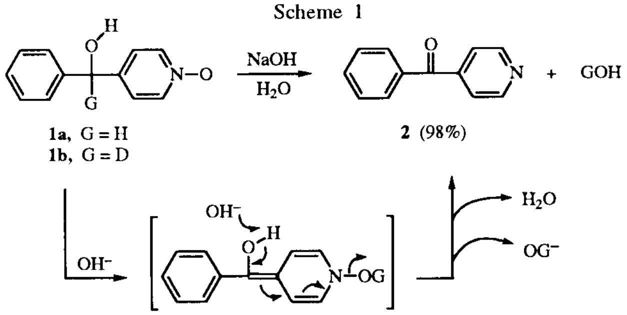
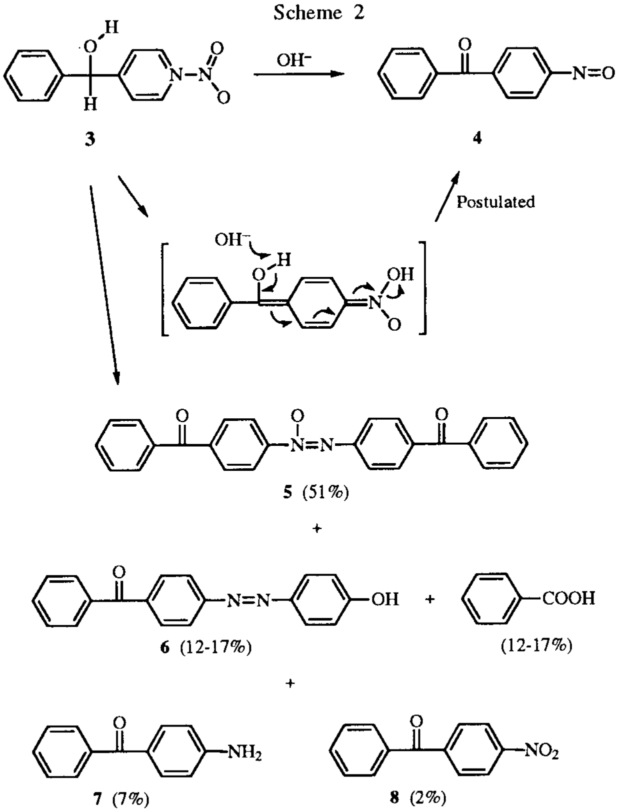
The impetus for this study came from the observation that **1a** underwent reaction with 1 *M* aqueous sodium hydroxide to yield 4-benzoylpyridine (**2**) (98%) [1]. Furthermore, when α-phenyl-α-deuterio-4-pyridinemethanol *N*-oxide (**1b**) was treated with sodium hydroxide in aqueous ethanol the rate of formation of ketone **2** was 1/3 as fast and the deuteron was removed irreversibly.

Scheme 1



We chose to examine the behavior of α-phenyl-4-nitrobenzenemethanol (**3**) with 1 *M* sodium hydroxide because the 4-pyridyl-*N*-oxide group in **1** and the *p*-nitrophenyl group of **3** can both be reduced and both are electron withdrawing. We postulated (Scheme 2) that **3** would undergo reaction with sodium hydroxide to yield *p*-nitrosobenzophenone (**4**), however, instead several products were isolated/detected as shown in Scheme 2. The principal product was 4,4'-dibenzoylazoxybenzene (**5**) (51%) [2]. Also isolated were benzoic acid (12%) and 4-hydroxy-4'-benzoylazobenzene (**6**) (12%) [3]. *p*-Aminobenzophenone (7%) and *p*-nitrobenzophenone (2%) and starting alcohol **3** (0.3%) were detected by pmr.

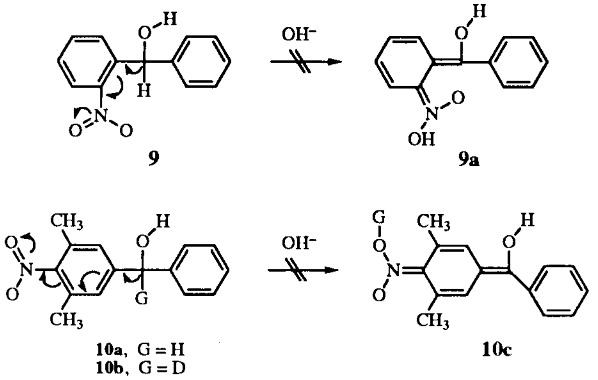
Scheme 2



Protiva *et al.* [4] reported that alcohol **3**, when heated under reflux with sodium amide and 2-dimethylaminochloroethane in benzene "apparently" produced azoxy **5** in 61% yield. Puckowski and Ross [5] obtained "varying yields" of **5** when they treated the monophthalate of alcohol **3** with ethanolic sodium hydroxide. Also, they reported that the monophthalate esters of both α-phenyl-2-nitrobenzenemethanol and α-phenyl-3-nitrobenzenemethanol underwent reaction with ethanolic sodium hydroxide without yielding any abnormal product.

In the present study neither α-phenyl-2-nitrobenzenemethanol (**9**) or α-phenyl-3-nitrobenzenemethanol underwent reaction with 1 *M* aqueous sodium hydroxide. The lack of reaction of the former was unexpected because the nitro group in the 2-and 4-positions would be expected to have similar electrical effects. We postulate for **9** that the redox reaction is impeded by steric inhibition of resonance in **9a**.

Scheme 3



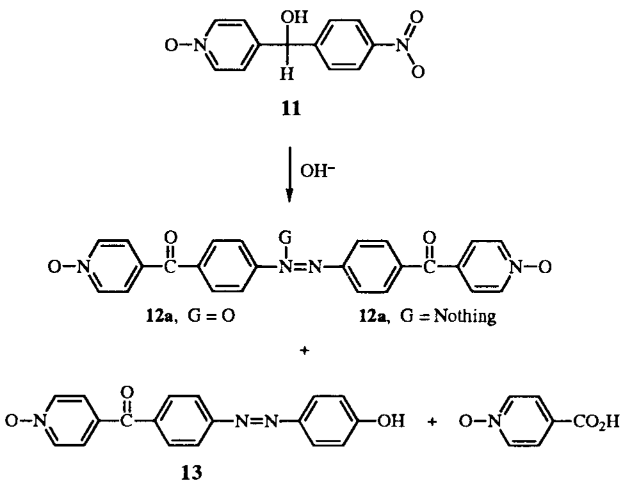
To test the hypothesis of steric inhibition of resonance [6] we treated α-phenyl-3,5-dimethyl-4-nitrobenzenemethanol (**10a**) [7] with 1 *M* sodium hydroxide (See Scheme 3). Compound **10a** also did not undergo reaction with 1 *M* sodium hydroxide. This lack of reactivity is attributed to steric inhibition of resonance in **10c**. When **10b** was treated with 1 *M* sodium hydroxide there was no deuteron loss which indicated that the deuteron was not removed in a reversible step and that the acidity of the deuteron had been reduced by the methyl groups *ortho* to the nitro group.

Since the 4-pyridyl-*N*-oxide group in **1** and the *p*-nitrophenyl group in **3** were both reduced while the alcohol in both was oxidized we chose to prepare α-(*p*-nitrophenyl)-4-pyridinemethanol *N*-oxide (**11**) as a compound to be treated with 1 *M* sodium hydroxide (see Scheme 4). Compound **11** when heated under reflux with 1 *M* sodium hydroxide yielded several products including 4,4'-bis(*p*-pyridoyl *N*-oxide)azobenzene (**12b**) (isolated) and the corresponding azoxy compound **12a** (detected by pmr). 4-Hydroxy-4'-(*p*-pyridoyl *N*-oxide)azobenzene (**13**) was isolated and isonicotinic acid *N*-oxide was detected by pmr. Furthermore, the infrared spectrum of the reaction mixture had no absorption to indicate a nitro group, **therefore the *p*-nitrophenyl group is involved in the sodium hydroxide-promoted redox reaction in preference to the 4-pyridyl *N*-oxide group**.

When α-(*p*-nitrophenyl)-4-pyridinemethanol (**14**) was heated under reflux with 1 *M* sodium hydroxide for 20 minutes the products isolated were 4,4'-bis(*p*-pyridoyl)-azoxybenzene (**15a**) and 4-hydroxy-4'-(*p*-pyridoyl)azobenzene (**16**), and isonicotinic acid was detected by pmr.

α-Methyl-4-nitrobenzenemethanol (**17**) when heated under reflux with 1 *M* sodium hydroxide did not undergo appreciable reaction.

Scheme 4



Table

Nitro Alcohols and 1 *M* Sodium Hydroxide

Alcohol	Reflux Time	Products
3	3 hours	Azoxy **5** (51%) Benzoic Acid (12%) Phenol **6** (12%) 4-Aminobenzophenone **7** (7%) [b] 4-Nitrobenzophenone (2%) [b]
11	10 minutes [a]	3:2 **azoxy-12a** to **azo-12b** (19% combined) [b] Phenol **13** (21%) Isonicotinic acid *N*-oxide [b]
11	14 minutes	1:1 **azoxy-12a** to **azo-12b** (27% combined) [b] Phenol **13** (33%)
14	20 minutes	**Azoxy-15b** (12-18%) Phenol **16** (20-35%) Isonicotinic acid [b]
17	3 hours	No reaction

[a] Quenched by adding hydrochloric acid. [b] From pmr.

The results of several of the reactions of the nitro alcohols are summarized in the Table.

We postulate the removal of a benzylic proton as the rate-determining step in these reactions because as the α-substituent was varied from methyl to phenyl to *p*-pyridyl to *p*-pyridyl *N*-oxide the rates of reactions increased (see Table for reaction times). This order is the same as the order of increasing electron-attracting ability of these groups, consequently, the acidity of the benzylic hydrogens in these compounds would be expected to increase in the same order. This with the irreversible removal of the benzylic proton support the postulate that the rate-determining step is the removal of a benzylic proton.

For α-phenyl-2-nitrobenzenemethanol (**9**) and for α-phenyl-3,5-dimethyl-4-nitrobenzenemethanols **10a** and **10b** where no reaction occurred we believe the necessary enols were not formed because of steric hindrance in the anion of the enols. Other examples of the influence of secondary steric hindrance on acidity have been reported [8]. When **10b** was treated with 1 *M* sodium hydroxide no deuterio-protio exchange occurred. This proved the removal of the benzylic deuteron was not reversible.

In retrospect it is not surprising that we did not isolate *p*-nitrosobenzophenone (**4**) from the reaction of **3** and sodium hydroxide because Barzaghi, Beltrame, Gamba, and Simonetta [9] were unable to isolate **4** as part of a systematic study, but they claimed they prepared the radical anion of **4** which dimerized to form **5**.

Our best evidence for having **4** as an intermediate came from the reaction of **3** with sodium hydroxide and an excess of aniline to yield a trace amount of 4-(*p*-benzoyl)azobenzene [10] and a much larger amount of **5**. We consider this azo compound to be a product of nitroso **4** and aniline [11a,b].

Nearly all of these reactions were done under an atmosphere of nitrogen, but oxygen did not appear to influence these reactions as oxygen did in the oxidation of *p*-nitrotoluene and derivatives in basic solution [12]. Alcohol **3** has been reported to undergo autooxidation with potassium *t*-butoxide in *t*-butyl alcohol [13], however, no azoxy or azo products were reported. In the present study when oxygen was present little or no autooxidation occurred.

It is noteworthy that 4-(*p*-nitrobenzoyl)pyridine [14] was prepared in nearly quantitative yield when 4-(*p*-nitrobenzyl)pyridine was treated with the stoichiometric amount of potassium permanganate and an improved isolation procedure was used. The treatment of 4-(*p*-nitrobenzoyl)pyridine with high quality sodium borohydride at room temperature produced alcohol **14** in high yield.

In a retromechanistic approach 4-hydroxy-4'-(*p*-pyridoyl-*N*-oxide)azobenzene (**13**) and isonicotinic acid *N*-oxide can be envisioned as being formed from 4,4'-bis-(*p*-pyridoyl-*N*-oxide)azobenzene (**12b**) (Scheme 4) in a Baeyer-Villiger oxidation involving hydrogen peroxide coming from hydroxy radical generated in a single electron transfer (set) reaction from the hydroxide ion [15]. Likewise, 4-hydroxy-4'-(*p*-pyridoyl)azobenzene (**16**) and isonicotinic acid can be conceived as products from 4,4'-bis(*p*-pyridoyl)azobenzene (**15b**) in a Baeyer-Villiger oxidation. Also, 4-hydroxy-4'-benzoylazobenzene (**6**) and benzoic acid may be envisioned as Baeyer-Villiger oxidation products. However, these pathways do not seem likely because neither 4,4'-bis(*p*-pyridoyl *N*-oxide) (**12b**) nor 4,4'-bis(*p*-pyridoyl)azoxybenzene (**15b**) underwent reaction with hydrogen peroxide in 1 *M* sodium hydroxide.

The product mixture from heating alcohol **11** with 1 *M* sodium hydroxide and sodium borohydride contained little or no phenol **13**. We postulate that sodium borohydride intercepts the intermediate that leads to **13** in the absence of sodium borohydride.

The isolation of 4-aminobenzophenone (**7**) was unexpected and it occurred in an unexpected manner: azoxy **5** was isolated from its reaction mixture by hot filtration and **7** precipitated when the filtrate from **5** cooled.

EXPERIMENTAL

All melting points are uncorrected. All elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Infrared spectra were recorded on Perkin-Elmer 1330 or a Beckman IR-8 Spectrometer. Proton magnetic resonance (pmr) spectra were obtained using a Joel-270 Spectrometer. Mass spectra were obtained using a Finnigan Mass Spectrometer Model 4021 and/ AEI MS 902/C15-2 V6 Datasptem 2040.

α-Phenyl-4-nitrobenzenemethanol (**3**) [14] was prepared by treatment of 4-nitrobenzophenone with sodium borohydride, mp 72-74° (from 2:1 benzene-cyclohexane). α-Phenyl-3-nitrobenzenemethanol [5] was prepared by treatment of 3-nitrobenzophenone with sodium borohydride: gray solid, mp 63-65° (from 2:1 benzene-cyclohexane). α-Phenyl-2-nitrobenzenemethanol was prepared by the method of Newman and Smith [17], mp 58-60°. α-Phenyl-3,5-dimethyl-4-nitrobenzenemethanol (**10a**), mp 61-63°, was prepared by the method of Goldstein and McNelis [7].

Improved Synthesis of 4-(*p*-Nitrobenzoyl)pyridine.

4-(*p*-Nitrobenzyl)pyridine [14] (19.7 g, 92 mmoles) was added with mechanical stirring to 19.3 g (122 mmoles) of potassium permanganate in 3.4 l of water. During 1 1/3 hours the temperature was raised to 89°. After 70 minutes a spot test using filter paper indicated no permanganate; during the next 10 minutes 2 additional 0.5 g quantities of potassium permanganate were added and negative tests for permanganate were obtained. To the mixture at 40-50° was added 500 ml of benzene. After the mixture was stirred for 1-2 minutes most of the benzene layer was transferred by suction-stick filtration to a separatory funnel and the aqueous layer in the separatory funnel was returned to the original mixture. This extraction operation was repeated twice using 200 and 100 ml of benzene. The combined benzene layers were successively filtered through Celite and Drierite and concentrated to yield 21 g (100%) of 4-(*p*-nitrobenzoyl)pyridine as a pale yellow solid, mp 118-121° [14] mp 121°); pmr (deuteriochloroform): δ 8.84 (d, 2H, *ortho* to ring N, J = 6.05), 8.34 (d, 2H, *ortho* to nitro, J = 8.98), 7.94 (d, 2H, *ortho* to carbonyl on ring with nitro, J = 8.98), 7.56 (d, 2H, *ortho* to carbonyl on pyr ring, J = 6.04); ir (chloroform): ν 1678 (carbonyl), 1530 and 1354 cm^{-1} (nitro).

α-(*p*-Nitrophenyl)-4-pyridinemethanol (**14**).

4-(*p*-Nitrobenzoyl)pyridine (11.4 g, 0.05 mole) in 275 ml of absolute ethanol was added during 15 minutes with stirring to 0.95 g (25 mmoles) of sodium borohydride in 120 ml of absolute ethanol. After the mixture was stirred an additional 2 hours 63 ml of 1 *M* hydrochloric acid was added; the light brown mixture became pale yellow and contained solid **1** which was collected by filtration. The filtrate was concentrated to about 150 ml and an equal volume of water was added as well as solid **1**. After 10 ml of concentrated ammonia water was added a pale yellow solid separated which was collected by filtration and was washed several times with water. The solid was stirred with 1 ml of concentrated ammonia water in 150 ml of water for 15 minutes, filtered, and dried. Yield of **14**: 10.7 g (93%), mp 161° red coloration. The pmr indicated good quality **14**.

Compound **14** was recrystallized 3 times (ethanol) to yield pale yellow crystals, mp 185-187° dec; ir (potassium bromide): ν 3100 (hydroxy), 1510 and 1340 cm^{-1} (nitro); pmr (perdeuteriomethanol): δ 8.47 (d, 2H, *ortho* to pyr N, J = 6.2), 8.21 (d, 2H, *ortho* to nitro, J = 8.8), 7.66 (d, 2H, *meta* to nitro, J = 8.4), 7.49 (d, 2H, *meta* to pyr N, J = 6.2), 5.91 (s, 1H, methynyl).

Anal. Calcd. for $C_{12}H_{10}N_2O_3$: C, 62.60; H, 4.38; N, 12.17. Found: C, 62.44; H, 4.62; N, 12.00.

α-(*p*-Nitrophenyl)-4-pyridinemethanol *N*-Oxide (**11**).

To 6.22 g (27 mmoles) of **14** in 150 ml of chloroform and 30 ml of 95% ethanol was added 7.2 g (65% purity, 27 mmoles) of *m*-chloroperoxybenzoic acid [18] in 140 ml of chloroform with stirring during 30 minutes. After 3 additional hours of stirring at room temperature 4.0 g of white solid was collected by filtration. The solid was recrystallized (methanol) to yield **11**, 3.43 g (52%) of nearly white crystals, mp 210-212° dec with prior softening; ir (potassium bromide): ν 3100 broad (hydroxy), 1510 and 1350 cm^{-1} (nitro); pmr (perdeuteriomethanol): δ 8.27 (d, 2H, *ortho* to N-O, J = 6.96), 8.23 (d, 2H, *ortho* to nitro, J = 8.79), 7.67 (d, 2H, *meta* to nitro, J = 8.79), 7.59 (d, 2H, *meta* to *N*-oxide, J = 7.14), 5.94 (s, 1H, methynyl).

Anal. Calcd. for $C_{12}H_{10}N_2O_4$: C, 58.54; H, 4.09; N, 11.38. Found: C, 58.48; H, 4.24; N, 11.26.

α-Phenyl-4-nitrobenzenemethanol (**3**) with Aqueous 1 *M* Sodium Hydroxide.

A mixture of 5.00 g (0.022 mole) of **3** and 150 ml of 1 *M* sodium hydroxide under nitrogen was stirred and heated under reflux for 3 hours. The mixture changed to pale yellow, to orange, and finally to dark red. The hot mixture was filtered to yield brownish-yellow solid (solid **1**) and filtate **1** (red). Solid **1** was washed several times with hot 1 *M* sodium hydroxide and then with hot water. Solid **1** was leached with boiling acetone, cooled, and filtered to yield 2.24 g (51%) of azoxy **5**, mp 199-201°. The filtrate from **5** was found (pmr) to have 4-aminobenzophenone, 4-nitrobenzophenone, azoxy **5**, and starting alcohol **3** in a 7:7:1:1, respectively. In another run the yield of purified **5** was 50%; pmr of **5** (recrystallized from benzene) (deuteriochloroform): δ 8.46 (d, 2H, *ortho* to N-O of azoxy, J = 8.79), 8.26 (d, 2H, *ortho* to N of azoxy, J = 8.61) 7.96 (d, 2H, *meta* to N-O of azoxy, J = 8.79), 7.94 (d, 2H *meta* to N of azoxy, J = 8.79), 7.84 (broad d, 4H, phenyl *ortho* to carbonyl), 7.59-7.68 (m, 2H, phenyl *para* to carbonyl), 7.48-7.56 (m, 4H, phenyl *meta* to carbonyl); ir (chloroform): ν 1661, 1600, 1461, and 1277 cm^{-1}.

After filtrate 1 was refrigerated an orange-red solid (solid **2**) was collected by filtration and the filtrate (filtrate **2**) was saved. Solid **2** (0.248 g) was impure 4-aminobenzophenone (**7**). From the pmr analyses of solid **2** and of the filtrate of purified azoxy **5** the yield of **7** was 7%.

Filtrate **2** was made acidic with hydrochloric acid to yield 0.782 g of red solid (solid **3**); a portion of solid **3** was recrystallized from ethanol to yield phenol **5** [3], mp 161-162.5°. An aliquot of solid **3** was leached with sodium bicarbonate. The leached solid (0.560 g, calculated) (17%) had ir and pmr spectra like that of **5** [3]. An aliquot of solid **3** was chromatographed (silica, ethyl acetate) to yield a 1:1 mixture (pmr) of benzoic acid and **5**. In another run the isolated yields of benzoic acid and **5** were each 12%; pmr of **6** (deuteriochloroform): δ 7.95 (s, 4H, arm center ring), 7.91 (d, 2H, phenyl *ortho* to azo, J = 8.8), 7.84 (d, 2H, phenyl *ortho* to carbonyl, J = 8.4), 7.62-7.48 (m, 3H, phenyl *p* and *m* to carbonyl), 6.98 (d, 2H, *ortho* to hydroxy, J = 8.4); ir (chloroform): ν 3588 (sharp), 3264 (broad), 1654 (carbonyl, strong), 1598 (strong), 1505, 1277 (strong), 1212 (strong), and 1137 (strong) cm^{-1}.

α-Phenyl-4-nitrobenzenemethanol (**3**) with 1 *M* Sodium Hydroxide and Aniline.

When 1.00 g (4.4 mmoles) of **3**, 2.0 ml of aniline, and 30 ml of 1 *M* sodium hydroxide were stirred and heated under reflux and under nitrogen for 3 hours a red oil was produced which when diluted with ethyl ether precipitated 0.072 g of **5** (based on mmp, ir, tlc). The ether portion was washed with 3 *M* hydrochloric acid, then with water, dried (magnesium sulfate), and concentrated. The residue was chromatographed on silica gel (methylene chloride): the fast moving zone was collected, concentrated (0.013 g) and rechromatographed on silica gel (methylene chloride). From this an orange solid was obtained: mp 84-86°; gc-ms analysis showed a 70:30 mixture of 4-benzoylazobenzene [10] and 4-nitrobenzophenone. Authenic 4-benzoylazobenzene and 4-nitrobenzophenone were used as reference compounds for the analysis.

α-(*p*-Nitrophenyl)-4-pyridinemethanol *N*-Oxide (**11**) with 1 *M* Sodium Hydroxide.

Compound **11** (0.996 g, 4.05 mmoles) and 50 ml of 1 *M* sodium hydroxide were stirred mechanically under nitrogen and were heated to reflux during 10 minutes and then under reflux for 10 minutes. By the time reflux had started a red solid was in suspension. The mixture was cooled with ice and 4 ml of concentrated hydrochloric acid was added. An orange-brown solid (solid **1**) was collected by filtration and was washed with 25-30 ml of ice water to yield a dark brown filtrate (filtrate **1**). Solid **1** was washed slowly with hot methanol (70 ml). Solid **1** (now light brown, 170 mg, mp 260-265°), was analyzed to be 3:2 azoxy **12a** to azo **12b** by pmr. The pmr was done in *ca* 5:3 wt/wt deuteriotrifluoroacetic acid-perdeuteriodimethyl sulfoxide; ref dimethyl sulfoxide: δ 8.58 (irregular d, *ortho* to *N*-oxide in both **12a** and **12b**, relative integration 3.43), 8.27 (d, 2H, *ortho* to N-O of azoxy, J = 8.8, relative integration 1.00), 8.02 (d, 2H, *ortho* to N of azoxy, J = 8.8, relative integration 1.10), 7.92-7.86 and 7.79-7.71 (multiplets, relative integration of the two 9.49). Combined yield of **12a** and **12b** was 170 mg (19%).

Analysis of foregoing data. Since the azoxy contribution to the δ 8.58 signal is twice the contribution of each of the azoxy signals at δ 8.27 and 8.02 the average of these contributions was multiplied by two to give the relative contribution of **12a** to the 8.58 signal. From these results the amounts of **12a** and **12b** were calculated to be 61% and 39%, respectively.

The methanol washings of solid **1** were concentrated to yield 232 mg of orange-red solid which was triturated with 1 *M* hydrochloric acid, filtered and washed with water to yield 0.137 g (21%) of 4-hydroxy-4'-(pyridoyl *N*-oxide)azobenzene (**13**), light orange solid, mp 271-274°, ir (potassium bromide): ν 3120, 2540, 1620, 1580, 1470, 1430, 1390, 1215, 1130, 930, 840, 620 cm^{-1}; ms: (70 eV) m/z 319 (8), 303 (4), 198 (2), 182 (3), 167 (2), 139 (2), 121 (51), 93 (100), 65 (38); pmr (trifluoroacetic acid-perdeuteriodimethyl sulfoxide, note: the ratio was not recorded; δ values vary with this ratio): δ 8.53 (d, 2H, *ortho* to *N*-oxide, J = 6.6), 7.92 (d, 2H, *meta* to phenol, J = 9.2), 7.84 (d, 2H, *meta* to *N*-oxide, J = 6.6), 7.78 (d, 2H, center ring *ortho* to azo, J = 8.8), 7.68 (d, 2H, center ring *ortho* to carbonyl, J = 8.8), 6.88 (d, 2H, *ortho* to phenol, J = 9.2). The analytical sample was leached with acetic acid, mp 279° dec.

Anal. Calcd: for $C_{18}H_{13}N_3O_3$: C, 67.71; H, 4.10; N, 13.16. Found: C, 67.42; H, 4.03; N, 12.96.

Filtrate **1** when concentrated yielded a dirty brown residue which was washed with 5-10 ml of water to yield filtrate **2** and a solid which was not identified. Filtrate **2** was concentrated to a residue which was leached with methanol. The leachings when concentrated yielded a dark brown gummy solid: pmr (perdeuteriomethanol): indicated a salt of isonicotinic acid δ 8.27 (d, 2H, *ortho* to N-O, J = 7.1), 7.91 (d, 2H, *ortho* to carboxylate, J = 7.1) with small amounts of other substances.

In another run in which the reflux time was 14 minutes the total yields of **12a** and **12b** in a 1:1 was 27% and the yield of phenol **13** was 33%. In this run no effort was made to analyze for isonicotinic acid *N*-oxide salt.

4,4'-Bis(*p*-Pyridoyl *N*-oxide)azobenzene (**12b**).

Forty ml of 0.36 *M* sodium hydroxide in isopropyl alcohol was flushed with nitrogen for 5 minutes before 1.001 g (4.07 mmoles) of *N*-oxide **11** was added. The mixture immediately turned green as stirring and heating were started; the mixture was heated under reflux for 5 minutes. The mixture was poured into 80 ml of water and cooled at 0°. A black solid was obtained by filtration which when dry was brownish-tan, 0.45 g, mp 263-266° dec. Recrystallization (acetic acid) yielded 0.368 g (43%) of **12b**, mp 261-262°; ir (potassium bromide): ν 1651 (carbonyl), 1263 cm^{-1} (*N*-oxide); pmr (deuteriotrifluoroacetic acid): δ 9.17 (d, 4H, *ortho* to *N*-oxide, J = 6.9), 8.50 (d, 4H, *meta* to *N*-oxide, J = 6.9), 8.36 (d, 4H, *ortho* to azo, J = 8.8), 8.27 (d, 4H, *ortho* to carbonyl, J = 8.5).

Anal. Calcd. for $C_{24}H_{16}N_4O_4$: C, 67.92; H, 3.80; N, 13.20; O, 15.08. Found: C, 67.40; H, 3.89; N, 12.94; O, 15.04.

α-(*p*-Nitrophenyl)-4-pyridinemethanol (**14**) with 1 *M* Sodium Hydroxide.

Compound **14** (1.15 g, 5 mmoles) was heated under reflux and stirred mechanically with 20 ml of 1 *M* sodium hydroxide for 1 hour. The mixture was filtered hot and the resulting solid was washed with 25 ml of hot 1 *M* sodium hydroxide to yield solid **1**. The original filtrate and the washings of solid **1** were combined and cooled to 0° to yield an orange solid which was collected by filtration (solid **2**).

Solid **1** was washed with 25 ml of boiling methanol to yield 186 mg (18%) of 4,4'-bis(*p*-pyridoyl)azoxybenzene (**15a**) plus a small amount of a substance believed to be the corresponding azo compound, **15b**. Solid **1** was identified as **15a**: pmr (deuteriochloroform): δ 8.87 (m, 4H, *ortho* to ring nitrogen), 8.50 (d, 2H *ortho* to nitrogen with oxygen of azoxy, J = 8.79), 8.27 (d, 2H, *ortho* to nitrogen without oxygen of azoxy, J = 8.79), 8.09 (d, small impurity), 7.96-8.01 (overlapping doublets, 4H, *meta* to azoxy, J = 8.98 and J = 8.79), 7.62-7.65 (m, 4H, *meta* to ring nitrogen); ir (potassium bromide): ν 1653, 1596, 1547, 1459, 1410, and 1285 cm^{-1}.

Compound **15a** was purified by successive crystallizations from dimethylformamide, chloroform, and dimethyl sulfoxide: orange powder, mp 232-234°.

Anal. Calcd. for $C_{24}H_{16}N_4O_3$: C, 70.58; H, 3.95; N, 13.72. Found: C, 70.30; H, 4.09; N, 13.55.

Solid **2** was crude 4-hydroxy-4'-(*p*-pyridoyl)azobenzene (**16**) based on pmr data. Solid **2** (103 mg) was leached with 8 ml of boiling acetic acid and filtered hot. The resulting pale orange solid was washed with ethyl ether and dried *in vacuo* to yield **16**: mp 301-303°; ir (potassium bromide): ν 3500-2600, 1654, 1588, 1480, 1433, 1277, 1134 cm^{-1}; pmr (deuteriotrifluoroacetic acid): δ 9.28 (d, 2H, *ortho* to nitrogen of pyridine, J = 6.19), 8.60 (d, 2H, *meta* to N of pyridine, J = 5.94), 8.52 (d, 2H, *meta* to hydroxy, J = 9.15), 8.38 and 8.32 (pair of doublets, 4H, center aromatic ring, J = 8.90 and J = 8.91), 7.51 (d, 2H, *ortho* to hydroxy, J = 9.40).

Anal. Calcd. for $C_{18}H_{13}O_2N_3$: C, 71.30; H, 4.32; N, 13.83. Found: C, 71.02; H, 4.49; N, 13.76.

The filtrate from solid **2** after standing yielded 0.2 g of brown solid which was not identified and filtrate **3**. Hydrochloric acid (1 *M*) was added to filtrate **3** to make the *p*H 5-6; a flocculant brown solid (not identified) was removed by filtration (filtrate **4**). Filtrate **4** was clarified by treatment with Celite and concentrated to dryness to yield 800 mg of solid **5**. A portion of solid **5** was leached with methanol and the leaching was concentrated to dryness; pmr of residue (perdeuteriomethanol with addition of sodium hydroxide pellet): was δ 8.56 (d, 2H, *ortho* to nitrogen, J = 6.04), 7.83 (d, 2H, *ortho* to carboxylate, J = 6.05); these values agree with values for sodium isonicotinate determined in our Laboratory.

4-(*p*-Nitrobenzoyl)pyridine *N*-Oxide.

By adapting the method of Craig and Purushothaman [18] 4.5 g (19 mmoles) of 4-(*p*-nitrobenzoyl)pyridine was converted to 2.4 g (50%) of 4-(*p*-nitrobenzoyl)pyridine *N*-oxide after recrystallization from acetone, light yellow crystals, mp 168-169.5° ir (potassium bromide): ν 1510 and 1340 (nitro), 1260 cm^{-1} (*N*-oxide); pmr (deuteriochloroform): δ 8.38 (d, 2H *ortho* to nitro, J = 8.8), 8.28 (d, 2H, *ortho* to *N*-oxide, J = 7.3), 7.92 (d, 2H, *ortho* to carbonyl in ring with nitro, J = 8.8), 7.72 (d, 2H, *ortho* to carbonyl in ring with *N*-oxide, J = 7.3).

In another run in which the crude product was purified by extraction with aqueous base instead of by chromatography the yield of recrystallized 4-(*p*-nitrobenzoyl)pyridine *N*-oxide (from acetone) was 60%.

Anal. Calcd. for $C_{12}H_8N_2O_4$: C, 59.01; H, 3.33; N, 11.47. Found: C, 59.18; H, 3.40; N, 11.50.

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REFERENCES AND NOTES

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