nitrobenzene giving yellow crystals, mp 167–168°. The yield of this reaction was 47%.

Anal. Calcd for $C_{16}H_{18}N_4O_6$: C, 53.03; H, 4.97; N, 15.47. Found: C, 52.87; H, 4.93; N, 15.17.

The nmr spectrum (DMSO) showed the following peaks in ppm from TMS: 3.32 (s, ≈6 H), 4.94 (m, ≈2 H), 6.95 (m, ≈2 H), and 7.53 (m, ≈8 H). The infrared spectrum (KBr) had the following bands: 2.88 μ (NH), 3.22 (aromatic CH), 3.36 (CH_3), 3.5 (OCH_3), 6.15 (C=C), 6.52 and 7.48 (NO_2), 6.73 (aromatic C=C), 8.93 (C-O-C), 9.5 (OCH_3), 11.6 (isolated arom. hydrogen), 12.6 (3 adjacent aromatic hydrogens), and 13.63 (aryl NO_2).

2,2'-Bis(1,2-dihydro-4-oxo-3,1-benzoxazine) (8).—Glyoxal, 21.8 g, aqueous 40%, 0.15 mol, was added dropwise to a hot solution of 41.1 g, 0.30 mol of *o*-aminobenzoic acid in 150 ml of hot dioxane. Cooling to room temperature and collecting several crops of white solid on a filter gave 19.8 g of product, mp 183–184°. The yield was 45%.

Anal. Calcd for $C_{16}H_{12}N_2O_4$: C, 64.86; H, 4.05; N, 9.46. Found: C, 64.74; H, 4.06; N, 9.16.

The infrared spectrum (KBr) was consistent with the assigned structure showing bands at 3.0 μ (NH), 5.83 (C=O), 6.65 (NH), 9.2 (C-O), and 13.4 (4 adjacent aromatic hydrogens).

N,N'-Bis(*o*-tolyl)ethylenediimine (9).—*o*-Toluidine, 32.1 g, 0.30 mol, was added dropwise to a stirred, warmed solution of glyoxal, 21.8 g, aqueous 40%, 0.15 mol, in 300 ml of methanol. Upon cooling a solid precipitated. Filtering and drying gave 18.6 g of yellow solid, mp 122–124° [lit.[8] 126.5–127.5°]. A second crop, 1.1 g, mp 122–124°, was afforded upon further cooling. The yield was 58%.

Anal. Calcd for $C_{16}H_{16}N_2$: C, 81.36; H, 6.78; N, 11.86. Found: C, 81.50; H, 6.77; N, 11.51.

The nmr spectrum ($CDCl_3$) exhibited the following peaks in ppm from TMS: 2.38 (s, 2.9 H), 7.20 (m, 4.2 H), 8.32 (s, 0.9 H). The infrared spectrum (KBr) had no NH or OH bands but had a strong band at 6.21 μ (C=N).

N,N'-Bis(*p*-tolyl)ethylenediimine (10).—Glyoxal, 14.3 g, aqueous 40%, 0.10 mol, was added dropwise to a cooled (0–10°) solution of *p*-toluidine, 21.4 g, 0.20 mol, in 100 ml of isopropyl alcohol. The resultant yellow solid was collected on a filter and quickly recrystallized from isopropyl alcohol. The recrystallized material was collected by filtration giving 6.2 g of yellow needles, mp 164–165°. The yield was 26%.

Anal. Calcd for $C_{16}H_{16}N_2$: C, 81.36; H, 6.78; N, 11.86. Found: C, 81.54; H, 6.55; N, 12.00.

The nmr spectrum ($CDCl_3$) had the following peaks in ppm from TMS: 2.37 (s, 3.2 H), 7.70 (s, 3.8 H), 8.38 (s, 0.9 H). The infrared spectrum (KBr) had a strong band at 6.20 μ (C=N).

N,N'-Bis(*p*-anisyl)ethylenediimine (11).—Glyoxal, 36.3 g, aqueous 40%, 0.25 mol, was added dropwise to a hot solution of 61.5 g, 0.50 mol, of *p*-anisidine in 300 ml of methyl alcohol. A solid soon precipitated and isopropyl alcohol was added and methanol distilled until solution occurred. Cooling to room temperature gave needles, which were collected on a filter and dried, 3.92 g, mp 153–154° [lit.[5] 159°], yield 58%.

The nmr spectrum ($CDCl_3$) shows the following peaks in ppm from TMS: 3.82 (s, 5.6 H) 7.13 (q of typical *p*-subst, 8.2 H), 8.42 (s, 2.0 H). The infrared spectrum (KBr) had a strong band at 6.23 μ (C=N).

N,N'-Bis(*p*-hydroxyphenyl)ethylenediimine (12).—Glyoxal, 72.5 g, aqueous 40%, 0.508 mol, was added dropwise to a stirred solution of *p*-aminophenol, 109.0 g, 1.0 mol, in 900 ml of refluxing methanol. A yellow precipitate soon formed and the mixture was cooled and filtered. The yellow solid thus collected was washed with methanol and dried giving 93.1 g of material, mp 185–186° dec. A small portion was recrystallized from isopropyl alcohol giving tan needles, mp 186° dec [lit.[3] 213–214°]. The yield was 86%.

Anal. Calcd for $C_{14}H_{12}N_2O_2$: C, 70.00; H, 5.00; N, 11.67; mol wt, 240.0899. Found: C, 70.07; H, 4.86; N, 11.40; mol wt, 240.0884 (mass spec.).

The nmr spectrum (DMSO) shows the following peaks in ppm from TMS: 7.18 (q, typical *para*-substituted, 7.8 H), 8.40 (s, 2.0 H), 9.75 (s, unresolved). The infrared spectrum (KBr) shows bands at 3.25 μ (hydrogen bonded OH), 6.21 (C=N), 7.9 and 8.07 (Ph-OH), and 12.3 (2 adjacent aromatic hydrogens).

N,N'-Bis(*p*-chlorophenyl)ethylenediimine (13).—A mixture of glyoxal, 14.5 g, aqueous 40%, 0.10 mol, and *p*-chloroaniline, 64.0 g, 0.5 mol, was stirred at 75° for 10 hr. The dark mixture was put on a rotary evaporator and water removed *in vacuo*. The resultant dark solid was then subjected to distillation at reduced pressure [80–90° (0.3 mm)] and unreacted *p*-chloroaniline was removed. The residue was taken up with hot isopropyl alcohol and cooled to give upon filtration 10.2 g of a purple solid, mp 107–110° dec. The yield was 37%.

Anal. Calcd for $C_{14}H_{10}N_2Cl_2$: C, 60.65; H, 3.61; N, 10.11; Cl, 25.63. Found: C, 60.74; H, 3.83; N, 9.80; Cl, 24.11.

The infrared spectrum (KBr) had bands at: 5.18 μ (C=N), 9.17 (*p*-Cl-Ph), 9.9 (*para*-substituted), and 12.3 (2 adjacent aromatic hydrogens). All the peaks in the nmr spectrum appeared as a complex multiplet in the aromatic region.

Perchloric acid titrations were carried out in the usual manner.[1b] The results were: compound (nitrogen equivalents per mole) 9 (2.02), 10 (1.15), 11 (1.17), 12 (1.03), 13 (0.91).

Registry No.—**1**, 4378-77-2; **2**, 24978-34-5; **3**, 24978-35-6; **4**, 25024-01-5; **5**, 24978-36-7; **6**, 24978-37-8; **7**, 24978-38-9; **8**, 24978-39-0; **9**, 24978-40-3; **10**, 24978-41-4; **11**, 24978-42-5; **12**, 24978-43-6; **13**, 24978-44-7; glyoxal, 107-22-2.

3-Nitromethylphthalide and 2-Phenyl-3-nitromethylphthalimidine

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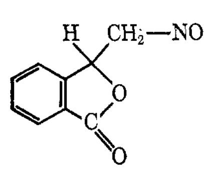
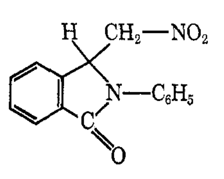
The product from the base-catalyzed condensation of *o*-phthalaldehydic acid and nitromethane, reported to be *o*-carboxy-β-nitrostyrene,[2] has been shown from its nuclear magnetic resonance (nmr) spectrum to be 3-nitromethylphthalide (I) as previously reported.[3,4] In a similar manner, the product from the condensation of 3-nitromethylphthalide and aniline, reported to be *o*-(2-nitrovinyl)benzanilide,[2] has been identified as 2-phenyl-3-nitromethylphthalimidine (II) from its nmr and infrared (ir) spectra.



I



II

The compound obtained from the condensation of *o*-phthalaldehydic acid and nitromethane was a white, colorless solid rather than the characteristic yellow of the unsaturated β-nitrostyrenes, its nmr spectrum in acetone lacked vinylic and carboxylic proton signals, and its ir spectrum lacked the OH stretching band. The nmr spectrum gives three sets of quartets attributed to nonaromatic protons centered at δ 6.29, 5.43, and 4.91 with each integrating to one proton relative to the aromatic proton signal (δ 7.81). The quar-

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[1] (a) Public Health Service Predoctoral Fellow 5-F01-GM-34,830; (b) abstracted in part from the Ph.D. Dissertation of B. D. Whelton, University of Washington, 1970; (c) to whom correspondence should be addressed.

[2] T. Hashimoto and S. Nagase, *Yakugaku Zasshi*, **80**, 1637 (1960); *Chem. Abstr.*, **55**, 7415*d* (1962).

[3] B. B. Dey and T. K. Srinivasan, *Arch. Pharm.* (Weinheim), **275**, 397 (1937).

[4] G. E. Ullyot, J. J. Stehle, C. L. Zirkle, R. L. Shriner, and F. J. Wolf, *J. Org. Chem.*, **10**, 429 (1945).

tets have been interpreted as arising from H-3, the hydrogen β to the nitro, and the two magnetically nonequivalent methylene protons α to the nitro group in 3-nitromethylphthalide. The nonequivalence results from unequal time average population of rotamers. The quartet at δ 6.29 results from the coupling of H-3 to the α protons by 7.8 and 3.0 Hz. Geminal coupling between the two nonequivalent α hydrogens is 14.3 Hz. Of these two, that which is downfield is then coupled to H-3 by 3.0 Hz and that which is upfield is coupled to H-3 by 7.8 Hz. The difference in coupling constants results from unequal average dihedral angles because of unequal time average populations of rotamers.

In an attempt to isolate the β-nitrostyrene, the work of Hashimoto and Nagase[2] was repeated for the synthesis of their reported *o*-(2-nitrovinyl)benzanilide. The product from the condensation of 3-nitromethylphthalide and aniline was recovered as a white, colorless solid. Its nmr displayed no vinylic or amide hydrogen signals and its ir lacked the amide NH stretching band. The same general nmr signal pattern was observed for this derivative in acetonitrile as was seen in the case of 3-nitromethylphthalide, and it has been concluded that the correct structure of this compound is 2-phenyl-3-nitromethylphthalimidine. Once again the α-methylene protons are magnetically nonequivalent being separated by ~0.27 ppm. They give two slightly overlapping quartets centered at δ 4.76 and 5.03 resulting from a geminal coupling of 13.5 Hz, and from a coupling of the α proton at lower field to H-3 by 4.3 Hz and that at higher field to H-3 by 4.6 Hz. The methine H-3 gives a triplet-like pattern at δ 5.83 resulting from coupling with the α hydrogens. The aromatic protons are observed as a complex multiplet centered at δ 7.56. Partial deuterium exchange of the α protons employing deuterium oxide and a catalytic amount of anhydrous potassium carbonate results in collapsing the signal attributed to H-3 to a singlet and in virtually eliminating the signal of the two α hydrogens. This confirms the assignment of the α-methylene hydrogens and the five-membered ring lactam. The result of the deuterium exchange on II also substantiates the structure of I because of the similarity in chemical shifts and multiplicities of the signals of the methine and methylene hydrogens in the two compounds.

Experimental Section[5]

3-Nitromethylphthalide.[2]—To a solution of 176.3 g (1.175 mol) of *o*-phthalaldehydic acid,[6] 72.4 g (1.18 mol) of nitromethane, and 885 ml of methanol cooled to $-15°$ was added dropwise and with stirring a solution of 112 g (2.78 mol) of sodium hydroxide in 400 ml of distilled water. After addition of the base, the solution was allowed to warm to 25° and stirred for 2.5 hr. The solution was then poured into 710 ml of 5 *N* hydrochloric acid with stirring. The product crystallized and was filtered and washed with distilled water. Additional cooling of the reaction mixture resulted in more crystalline material. The combined product was dissolved in 2-propanol and recrystallized to give 140.4 g (61%) of white crystals: mp 129–131° (Fisher-Johns) (lit. mp 129–130°,[2] 130°,[3] 130–131°[4]); ir (KBr) 1560 (NO_2), 1755 (lactone C=O), 2980 (aliphatic CH), and 3040 cm^{-1} (aromatic CH).

2-Phenyl-3-nitromethylpythalimidine.[2]—A solution of 5.0 g (26.0 mmol) of 3-nitromethylphthalide and 4.65 g (50.0 mmol) of aniline was refluxed in 10 ml of anhydrous toluene for 18 hr. The reaction mixture was diluted with benzene and extracted three times with 0.6 *N* hydrochloric acid. After washing the organic layer with distilled water to pH 5.5 and drying over anhydrous sodium sulfate, the solvents were evaporated and the remaining oil dissolved in 2-propanol. Repeated recrystallization gave 4.6 g (66%) of white crystals: mp 158.0–159.0° (Kofler) (lit.[2] mp 151–153°); ir (KBr) 1380 and 1540 (NO_2), 1685 (lactam C=O), 2920 (aliphatic CH), and 3060 cm^{-1} (aromatic CH).

Anal. Calcd for $C_{15}H_{12}N_2O_3$: C, 67.16; H, 4.51; N, 10.44. Found: C, 67.03; H, 4.38; N, 10.64.

Registry No.—I, 3598-68-3; II, 25097-57-8.

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[5] All nmr spectra were recorded on a Varian A-60 spectrometer at operating temperature of about 37° utilizing ~20% solutions of compound with tetramethylsilane (TMS) as the internal reference. Infrared spectra were determined using a Beckman IR 5-A infrared spectrophotometer. All melting points are uncorrected.

[6] R. L. Shriner and F. J. Wolf, "Organic Syntheses," Col. Vol. III, Wiley, New York, N. Y., 1955, p 737.

Basicity of N-Ylides[1]

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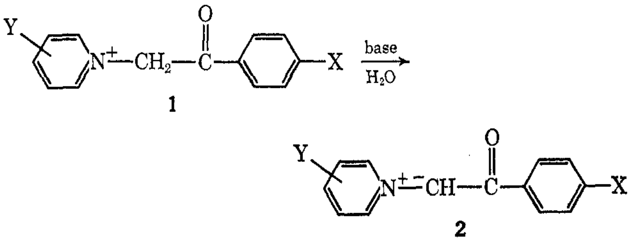
Although nitrogen ylides were isolated and characterized by Krohnke[2] over 30 years ago, no systematic study of the basicities of these ylides has been reported. The basicity trends are significant in that they suggest to some extent the expected nucleophilic reactivity and delineate the factors which are important in this respect in ylide structures. Also nitrogen ylides are unique in that they can derive no stabilization by d-orbital carbanion delocalization, a usually important factor in the better known sulfur and phosphorus ylides. We have determined the pK_a's of a number of pyridinium (**1**) and ammonium salts in order to determine to some extent the significant factors affecting the stability and reactivity of the corresponding ylide (**2**).



The pK_a's of a number of pyridinium salts are listed in Table I. In cases where the pyridinium salt was not acidic enough to conveniently titrate with aqueous sodium hydroxide solution, the pK_a was determined by titrating the isolated ylide with aqueous hydrochloric acid. In preparative runs, the ylides were isolated by employing sodium carbonate as the base (see Table II).

Table III summarizes the results of the $\sigma\rho$ treatments of the pK_a's. When the phenacyl substituent X is held at H, NO_2, or halogen and the pyridine substituent Y is varied, ρ is fairly constant and equals an average of 2.9. This indicates that electron-withdrawing substituents on the pyridine nucleus tend to stabilize the ylide. An inductive effect is certainly one reason for the moderately high ρ value. An additional

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[1] For a previous paper in this series, see W. G. Phillips and K. W. Ratts, *Tetrahedron Lett.*, 1383 (1969).

[2] F. Krohnke, *Chem. Ber.*, **68**, 1177 (1935).