from aryl amines and dimethyl acetylenedicarboxylate (2)[5,9] or aryl amines and ethyl ethoxalylacetate (1), were intimately mixed with 0.04 mol of the same aryl amine and heated to reflux for 10 min. The hot melt was cooled to room temperature and the resulting crystals thoroughly triturated with cold methanol. The maleimides were virtually insoluble in methanol but could be purified by sublimation [200° (0.1 mm)] or by recrystallization from acetic acid.

Method B.—The dimethyl acetylenedicarboxylate (0.01 mol) was added to 0.05 mol of the aryl amine and the initially vigorous reaction allowed to subside. The medium was then heated at reflux for 10 min and the maleimide product isolated as above.

Method C.—A solution of 0.01 mol of the appropriate anilinofumarate, synthesized as described by Huisgen,[5] was prepared in 100 ml of anhydrous methanol. The solution was saturated with anhydrous ammonia gas at 0° and sealed. After standing at room temperature for 1 week it was opened, resaturated with ammonia, and sealed for an additional week. The methanol was then chilled and the precipitated maleimide filtered off, dried, and sublimed *in vacuo*.

Dimethyl 4-Chlorophenoxyfumarate.—Following the procedure outlined for phenol,[14] 4-chlorophenol (30 mmol) was dissolved in 25 ml of ether containing 30 mmol of N-methylmorpholine. To this solution was added 30 mmol of **2** dissolved in 25 ml of ether. The mixture was allowed to stand at room temperature for 3 days, the ether removed by distillation, and the oily residue dissolved in benzene. The benzene phase was washed well with water, dried ($MgSO_4$), and concentrated to an oil which on cooling deposited 3.08 g (38%) of pale yellow crystals. An analytical sample was prepared by recrystallization from 1:1 benzene:hexane: mp 57–59°; ir (Nujol mull) 1740 and 1725 (C=O) and 1660 cm^{-1} (C=C); nmr ($CDCl_3$) δ 3.67 (s, 3, OCH_3), 3.72 (s, 3, OCH_3), 6.60[15] (s, 1, =CHCOOCH$_3$), and 6.8 to 7.4 ppm (m, 4, ArH).

Anal. Calcd for $C_{12}H_{11}ClO_5$: C, 53.33; H, 4.07. Found: C, 53.42; H, 4.10.

Reaction of this 4-chlorophenoxy adduct with *p*-anisidine according to Method A gave a 57% yield of **4b**.

Registry No.—**4a**, 25024-00-4; **4b**, 24978-24-3; **4c**, 24978-25-4; **4d**, 24978-26-5; **4e**, 24978-27-6; **4f**, 13797-26-7; **5a**, 24978-29-8; **5b**, 24978-30-1; **5c**, 17244-42-7; dimethyl 4-chlorophenoxyfumarate, 24355-81-5.

(14) E. Winterfeldt and H. Preuss, *Chem. Ber.*, **99**, 450 (1966).

(15) The observation that fumarate vinyls in phenoxy adducts fall at δ 6.45–6.68 ppm while maleate vinyls appear at 5.00–5.05 ppm permits assignment of fumarate geometry to this material. See ref 14 and N. D. Heindel and L. A. Schaeffer, *J. Org. Chem.*, in press, for similar examples.

Glyoxal Derivatives. II. Reaction of Glyoxal with Aromatic Primary Amines

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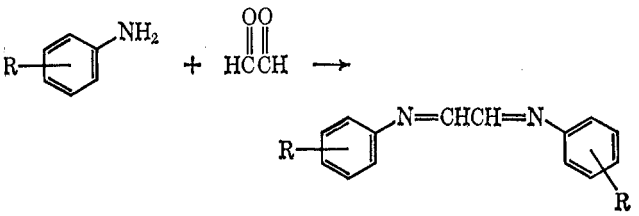
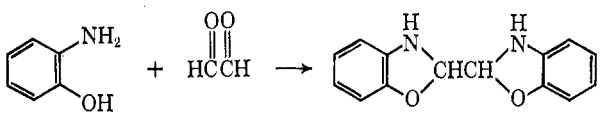
We have recently reported on the reaction of glyoxal with aromatic and aliphatic primary amines.[1] In that case, the products were N-substituted 1,2-diimines. In this paper we continue with our observations on the reaction of aromatic primary amines with glyoxal.

In earlier work it has been found that *p*-(N,N-dimethylamino)aniline,[2] *p*-aminophenol,[3] 2-hydroxy-5-chloroaniline, and 2-hydroxy-5-nitroaniline[4] react with glyoxal to give N-substituted aromatic 1,2-diimines.



Chwala and Bartek[5] report that *p*-anisidine and glyoxal sulfate react in the presence of sodium acetate to give the diimine corresponding to the above 1,2-diimines. Bayer has reported that *o*-aminophenol gave a 1,2-diimine;[6] however, Murase demonstrated that it was actually a cyclization product.[3]



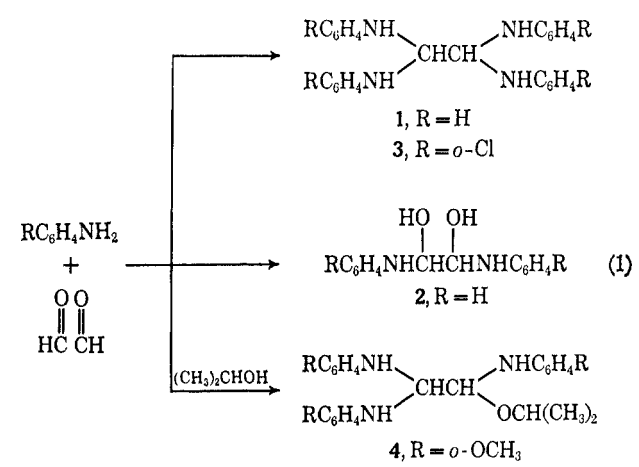
Other reports[7,8] state that aniline and glyoxal give only tars.

Somewhat related is the report by Malik, *et al.*,[9] that phenylglyoxal hydrate reacts with various aromatic primary amines to give imines; however, Proctor and Rehman offer evidence that the products are actually α-diamines or products incorporating alcohol solvent.[10]

Results and Discussion

We have found that aromatic primary amines react with 40% aqueous glyoxal to give either 1,2-diimines, 1,2-dihydroxy-1,2-diamino compounds, or tri- and tetraaminoethane derivatives. Thus, glyoxal reacts with excess aniline in isopropyl alcohol to give a 47% yield of 1,1′,2,2′-tetrakis(phenylamino)ethane, **1**, or with two molar equivalents of aniline to give 1,2-bis(phenylamino)-1,2-dihydroxyethane, **2**, in 54% yield.

Similarly, *o*-chloroaniline reacts with glyoxal giving a 47% yield of 1,1′,2,2′-tetrakis(*o*-chlorophenylamino)-ethane, **3**, and *o*-anisidine gives 1,1′,2-tris(*o*-methoxyphenylamino)-2-isopropoxyethane, **4**, in 41% yield when the reaction is carried out in isopropyl alcohol solvent. These reactions are summarized in eq 1.



(4) O. Leminger and M. Farsky, *Collect. Czech. Chem. Commun.*, **30**, 607 (1965).

(5) A. Chwala and W. Bartek, *Monatsh. Chem.*, **82**, 652 (1951).

(6) E. Bayer, *Chem. Ber.*, **90**, 2325 (1957).

(7) I. S. Bengelsdorf, *J. Amer. Chem. Soc.*, **75**, 3138 (1953).

(8) S. B. Needleman and M. C. C. Kuo, *Chem. Rev.*, **62**, 422 (1962).

(9) W. U. Malik, D. R. Gupta, and C. L. Taploo, *J. Chem. Eng. Data*, **11** (2), 211 (1966).

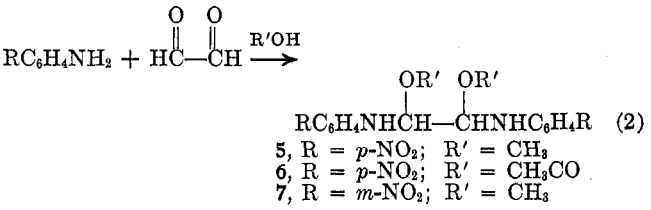
(10) G. R. Proctor and M. A. Rehman, *J. Chem. Soc. C*, **1967** (2696).

(1) (a) Preliminary communication: J. M. Kliegman and R. K. Barnes, *Tetrahedron Lett.*, 1953 (1969); (b) J. M. Kliegman and R. K. Barnes, *Tetrahedron*, in press.

(2) Y. Tominatsu, *Yakugaku. Zasshi*, **77**, 292 (1957).

(3) I. Murase, *Bull. Chem. Soc. Jap.*, **32**, 827 (1959).

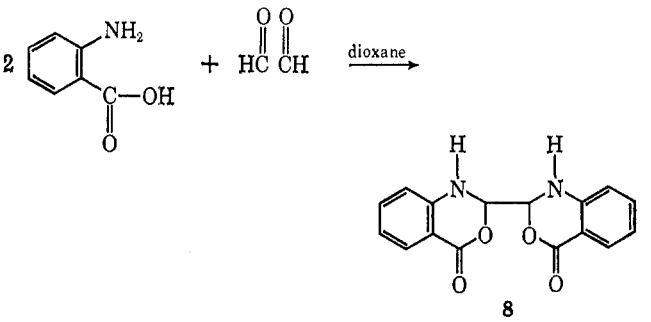
Ethylene glycol derivatives similar to compound 2 were also obtained from nitroanilines. *p*-Nitroaniline reacts with glyoxal in methyl alcohol to give a 32% yield of 1,2-bis(*p*-nitrophenylamino)-1,2-dimethoxyethane, **5**, while in acetic acid solvent the product is 1,2-bis(*p*-nitrophenylamino)-1,2-diacetoxyethane, **6**, in 77% yield. Glyoxal reacts with *m*-nitroaniline in methyl alcohol to give a 45% yield of 1,2-bis(*m*-nitrophenylamino)-1,2-dimethoxyethane, **7**. No diimines were isolated from these reaction mixtures. Equation 2 summarizes the above.



$$RC_6H_4NH_2 + HC(=O)-CH(=O) \xrightarrow{R'OH} RC_6H_4NHCH(OR')-CH(OR')NHC_6H_4R \quad (2)$$

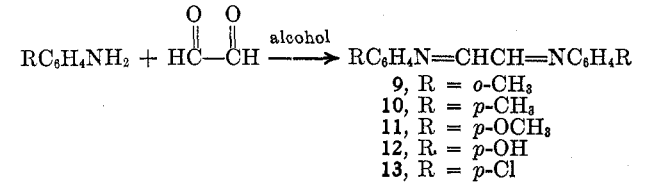
5, R = *p*-NO_2; R′ = CH_3
6, R = *p*-NO_2; R′ = CH_3CO
7, R = *m*-NO_2; R′ = CH_3

The observation by Murase[3] that *o*-aminophenol gave a cyclic product with glyoxal led us to investigate the similar reaction of glyoxal with *o*-aminobenzoic acid. In this reaction, a 45% yield of 2,2′-bis(1,2-dihydro-4-oxo-3,1-benzoxazine), **8**, is realized in which self incorporation of the hydroxylic moiety takes place.



8

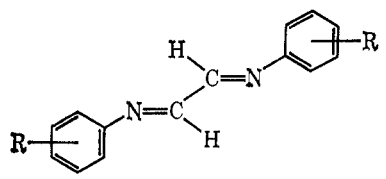
Schiff base formation was the primary mode of reaction for the other aromatic primary amines noted in this study. Thus, *o*-toluidine (**9**, 70% yield), *p*-toluidine (**10**, 26% yield), *p*-anisidine (**11**, 58% yield), *p*-hydroxyaniline[3] (**12**, 37% yield), and *p*-chloroaniline (**13**, 78% yield) all gave the corresponding 1,2-diimine when the reaction was carried out in either methanol or isopropyl alcohol.



$$RC_6H_4NH_2 + HC(=O)-CH(=O) \xrightarrow{\text{alcohol}} RC_6H_4N{=}CHCH{=}NC_6H_4R$$

9, R = *o*-CH_3
10, R = *p*-CH_3
11, R = *p*-OCH_3
12, R = *p*-OH
13, R = *p*-Cl

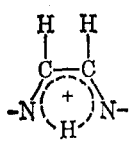
There is considerable evidence that aromatic aldimines in which the carbon–nitrogen double bond is conjugated with an aromatic ring exist preferentially in the *E*[11] conformation.[12,13] This observation is paralleled in the case of diimines **9–13**. An inspection of molecular models of compound **9**, for example, shows that only the *E-s-cis-E* or *E-s-trans-E* conformations allow for coplanarity of the aromatic rings with the two carbon–nitrogen double bonds, thereby extending the conjugated system. This fact, coupled with the greater stability associated with the *s-trans* configuration in 1,3-diene systems leads to the conclusion that these diimines should all exist in the *E-s-trans-E* conformation, **14**.



14

The nmr spectra of compounds **9–12** support this conclusion and have been discussed previously.[1a] The behavior of compounds **9–13** toward 0.1 *N* perchloric acid in acetic acid complements their conformational assignments. Thus, we find that compounds **10–13** all titrate for one molar equivalent of nitrogen, whereas, compound **9** titrates for two.

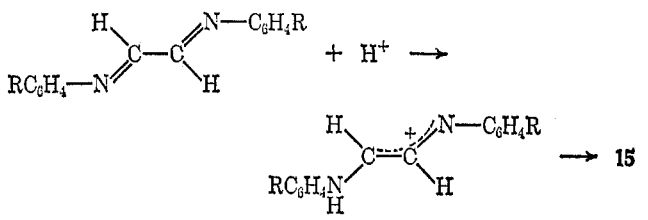
We have proposed that in the case of aliphatic 1,2-diimines, monobasic behavior towards perchloric acid is due to formation of a five-membered, highly stabilized, planar ring system[1] such as **15**.



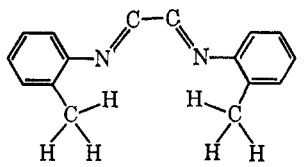
15

Such highly stabilized systems are only possible if the 1,2-diimine can assume an *E-s-cis-E* conformation (*Z-s-cis-Z* and *E-s-cis-Z* being too sterically hindered to allow a single proton to interact with both nitrogens).

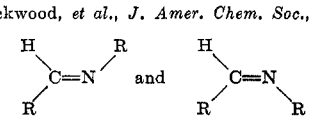
The analogous situation exists with compounds **10–13**. The only conformation which allows for protonation followed by rotation to the planar, cyclic *s-cis* configuration is the *E-s-trans-E* structure (the *E-s-cis-E* would already be in the proper configuration).



An inspection of molecular models of compound **9** demonstrates why it is, on the other hand, dibasic toward perchloric acid. The bulkiness of the *o*-methyl group is such that, when it assumes a planar *E-s-cis-E* conformation, the nitrogens are blocked from interaction with the proton. The molecule cannot, then,



(11) J. E. Blackwood, *et al.*, *J. Amer. Chem. Soc.*, **90**, 510 (1968); *i.e.*,

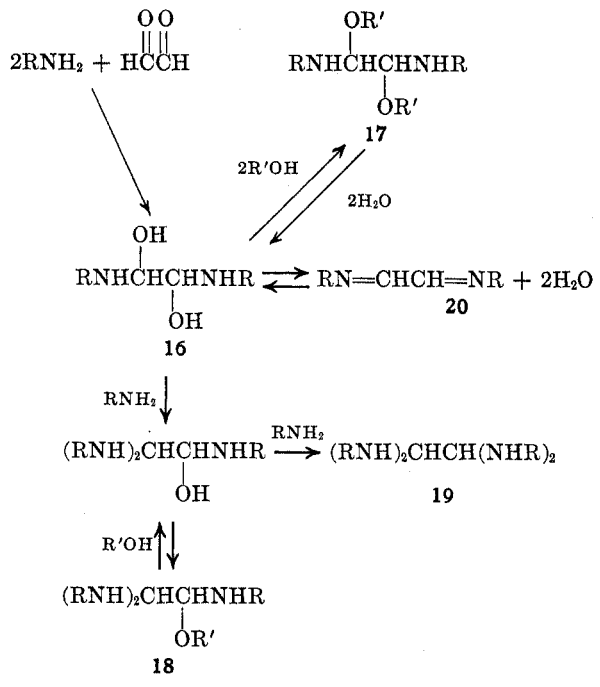


are *E* and *Z*, respectively, while *s-cis* and *s-trans* refer to tortional isomers around the central carbon–carbon bond of the 1,3-diene.

(12) V. De Goauck and R. J. W. LeFevre, *J. Chem. Soc.*, 741 (1938).

(13) D. G. Anderson and G. Wettermark, *J. Amer. Chem. Soc.*, **87**, 1433 (1965).

SCHEME I



assume the five-membered ring configuration and should act as a "normal" diimino compound[14] and take up the second mole of perchloric acid.

The ultraviolet spectra of these Schiff bases are in agreement with the proposed structures and are given in Table I.

TABLE I
UV SPECTRA OF 1,2-DIIMINES[a]

Compd	λmax, mμ (log ε)		
9	242 (4.06)	273 (3.99)	380 (4.25)
10	235 (4.23)	300 (3.88)	380 (3.93)
11	240 (4.12)	290 (3.99)	350 (4.19)
12	235 (4.10)	300 (3.81)	387 (4.29)
13	255 (4.41)	290 (3.81)	430 (3.32)

[a] 95% EtOH.

It is difficult to completely understand what the driving forces are for formation of the observed products in these reactions. The large number of variables coupled with differences in reaction condition and incomplete product balances makes speculation hazardous. One set of equilibria that would explain the products which we observed is as follows in Scheme I.

Experimental Section[15]

1,1',2,2'-Tetrakis(phenylamino)ethane (1).—Glyoxal, 14.5 g, aqueous 40%, 0.10 mol, was added slowly at 0–10° to aniline, 37.2 g, 0.40 mol, dissolved in 100 ml of isopropyl alcohol. In about 15 min the total reaction mixture became a white paste. Filtering and drying the product *in vacuo* gave a white solid, 20.0 g, mp 87–92°, 50% yield. Recrystallization from isopropyl alcohol gave 17.5 g material, 47% yield, with a melting point of 101–102°.

Anal. Calcd for $C_{26}H_{26}N_4$: C, 79.17; H, 6.64; N, 14.20. Found: C, 78.88; H, 6.85; N, 14.30.

The infrared spectrum (KBr) had a band at 2.97 μ (NH) and no bands indicating the presence of OH or C=N.

1,2-Bis(phenylamino)-1,2-dihydroxyethane (2).—When the reaction forming compound 1 above was conducted with 0.21 mol of aniline, 19.5 g, and 0.10 mol of glyoxal, 14.5 g, aqueous 40%, the major product was compound 2, 13.0 g, mp 106°, after recrystallization from cyclohexane, 54% yield..

Anal. Calcd for $C_{14}H_{16}N_2O_2$: C, 68.80; H, 6.60; N, 11.46. Found: C, 69.02; H, 6.53; N, 11.44.

The infrared spectrum (KBr) of this compound had bands at 3.02 μ (NH), 3.15 (OH), and 9.97, 10.1 (C–OH).

1,1',2,2'-Tetrakis(*o*-chlorophenylamino)ethane (3).—Glyoxal, 14.5 g, aqueous 40%, 0.10 mol, was added dropwise to *o*-chloroaniline, 64.0 g, 0.5 mol, with vigorous stirring. After several hours a water layer separated and the mixture was put on a rotary evaporator and water removed *in vacuo*. Distillation of the dark brown mixture afforded only unreacted *o*-chloroaniline, 7.0 g, 27° (0.05 mm), $\eta^{25}D$ 1.5863, leaving a semisolid residue. Trituration of this with isopropyl alcohol gave a yellow solid which was collected on a filter, 24.9 g, mp 131–133° dec, 47% yield.

Anal. Calcd for $C_{26}H_{22}N_4Cl_4$: C, 58.65; H, 4.14; N, 10.52; Cl, 26.69. Found: C, 58.79; H, 3.86; N, 10.20; Cl, 27.08.

The infrared spectrum (KBr) had the following major bands: 2.93 and 2.97μ (NH), 6.64 (arom and NH), and 13.45 (4 adjacent aromatic hydrogens).

1,1',2-Tris-(*o*-methoxyphenylamino)-2-isopropoxyethane (4)—Glyoxal, 21.8 g, aqueous 40%, 0.15 mol, was added dropwise to a hot, stirred solution of *o*-anisidine, 36.9 g, 0.30 mol, in 200 ml of isopropyl alcohol. After several days a dark orange solid precipitated which was collected by filtration and recrystallized from isopropyl alcohol to give 18.4 g of dark solid. This was crushed in a mortar and dried *in vacuo*, mp 70–71°. The yield was 41%.

Anal. Calcd for $C_{26}H_{33}N_3O_4$: C, 69.18; H, 7.32; N, 9.31. Observed: C, 68.82; H, 7.63; N, 9.20.

The infrared spectrum (KBr) had bands at 2.9 μ (NH), 3.52 (OCH_3), 8.05 and 8.17 (Ph–O–), 8.50 ($CH(CH_3)_2$), 8.93 (aliphatic C–O–C), 9.73 (OCH_3), and 13.55 (4 adjacent aromatic hydrogens).

1,2-Bis(*p*-nitrophenylamino)-1,2-dimethoxyethane (5).—Glyoxal, 36.3 g, aqueous 40%, 0.25 mol, was added dropwise to a stirred, refluxing solution of *p*-nitroaniline, 69.0 g, 0.50 mol, in 500 ml of methyl alcohol. After addition was complete the solution was allowed to cool to room temperature and was filtered giving 5.4 g of an olive colored solid, mp 172–174°. The mother liquors were reduced in volume by one-half and cooled. Filtering and washing with ether gave 23.5 g of a bright yellow solid, mp 172–173°. Total yield was 32%.

Anal. Calcd for $C_{16}H_{18}N_4O_6$: C, 53.04; H, 4.97; N, 15.46. Found: C, 52.64; H, 4.95; N, 15.42.

The nmr spectrum (DMF) exhibited the following peaks in ppm from TMS: 3.45 (s, 6.1 H), 5.17 (d, J = 8.0 cps, 1.8 H), 7.45 (d, J = 8.0 cps, 1.8 H), 7.60 (8 for typical *p*-subst, 8.0 H). The infrared spectrum (KBr) had bands at 2.93 μ (NH), 3.50 (OCH_3), and 8.99 (aliphatic C–O–C), besides typical aromatic bands.

1,2-Bis(*p*-nitrophenylamino)-1,2-diacetoxyethane (6).—Glyoxal, 5.37 g, aqueous 40%, 0.037 mol, in 5 ml of glacial acetic acid was added to a hot solution of *p*-nitroaniline, 10.1 g, 0.073 mol, in 150 ml of hot acetic acid. The resultant mixture was heated to reflux and filtered. Upon cooling a solid precipitated. Filtration and drying gave 5.6 g of a dark brown solid, mp 237–240° dec. The mother liquors were reduced in volume by one-half and the solution cooled. This afforded upon filtration 0.83 g of additional solid. The total yield was 77%.

Anal. Calcd for $C_{18}H_{18}N_4O_8$: C, 51.67; H, 4.31; N, 13.40. Found: C, 52.02; H, 4.13; N, 13.71.

The nmr spectrum (DMSO) was not definitive; however, acetoxy methyl protons were clearly evident. The infrared spectrum showed bands at 2.97 μ (NH), 3.24 (aromatic), 5.83 (C=O), in addition to other aromatic and nitro peaks.

1,2-Bis(*m*-nitrophenylamino)-1,2-dimethoxyethane (7)—Glyoxal, 21.8 g, aqueous 40%, 0.15 mol, was added dropwise to a hot, stirred solution of 41.4 g, 0.30 mol of *m*-nitroaniline in 300 ml of methyl alcohol. After addition was complete the resultant solution was heated to reflux and then cooled in a refrigerator (−15°). Filtration of the resulting mixture afforded 25.2 g yellow solid, mp 163–164°. A small portion was recrystallized from methanol–

(14) For example, N,N'-dibenzylidineethylenediamine adds 2 mol of perchloric acid.

(15) Melting points and boiling points are uncorrected. Infrared, ultraviolet, nuclear magnetic resonance, and mass spectra were obtained in Perkin-Elmer Model 21 and Bairde Model 4SS, Cary Model 14, Varian A60, and AIC MS-9 spectrophotometers by Messrs. W. H. Joyce, C. M. Lovell, C. B. Strow, Jr., and B. E. Wilkes. Microanalyses were performed by Mr. S. Gottlieb and his associates.

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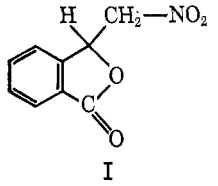
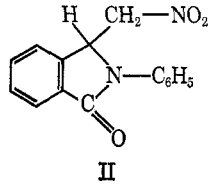
The product from the base-catalyzed condensation of *o*-phthalaldehydic acid and nitromethane, reported to be *o*-carboxy-β-nitrostyrene,[2] has been shown from its nuclear magnetic resonance (nmr) spectrum to be 3-nitromethylphthalide (I) as previously reported.[3,4] In a similar manner, the product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