was diluted with 25 ml. of water. The precipitated product weighed 0.9 g. (39%), m.p. 193° dec. Recrystallization from methoxyethanol raised the melting point to 201° dec.

The n.m.r. spectrum of this compound in dimethyl sulfoxide-d_6 was essentially identical with that of 2-amino-4-dichloromethyl-6-methyl-*s*-triazine.

Isomerization of XIII to X.—A mixture of 6.0 g. of XIII, 1.2 g. of 2,4-diamino-6-methyl-*s*-triazine, and 25 ml. of dimethylformamide was heated for 45 min. at 100°. Water then was added to the point of beginning crystallization. The crude product obtained was triturated with methoxyethanol which left 1.0 g., m.p. 126–130°, identified by infrared comparison as X.

Reduction of X to XLI.—A solution of 15 g. (0.025 mole) of X in 100 ml. of acetone was added to 150 g. (1.0 mole) of sodium iodide in 50 ml. of acetic acid and 500 ml. of acetone. After 6 min. at room temperature the reaction mixture was added to 25 g. of sodium bisulfite in 1 l. of ice–water. By extraction with ether, 7.2 g. of a dark oil was recovered. This was crystallized in part from ethanol, giving 3.4 g. of crude XLI, m.p. 79–85° (31% yield). Recrystallization from cyclohexane raised the melting point to 87–88.5°.

The n.m.r. spectrum of this compound was consistent with the structure XLI, although there was evidence for a minor amount of an impurity containing $-CH_2Br$.

2,4-Dimethoxy-6-methyl-*s*-triazine (XLII).—A solution of 16.5 g. (0.050 mole) of IX and 5.4 g. (0.10 mole) of sodium methoxide in 115 ml. of methanol was stored at room temperature for 60 hr. Only 1.2 g. of sodium chloride was obtained. The solution was saturated with carbon dioxide to precipitate the residual alkoxide, was filtered, and then was evaporated as completely as possible. The residue was extracted with an ether–petroleum ether mixture from which 4.7 g. of crystals were recovered, m.p. 45°. Recrystallization from hexane raised the melting point to 62–64°; the crude yield was 61%.

2-Methoxy-4-methyl-6-trichloromethyl-*s*-triazine (XLIII).—A mixture of 15 g. of IX, 18 ml. of triethylamine, and 75 ml. of methanol was heated at reflux for 6 hr. The solvent then was evaporated, and the residue was extracted with ether. The ether solution was distilled, giving 5.5 g. of product boiling at about 120° (6 mm.). The product was shown to be the expected[34c] XLIII by n.m.r. spectroscopy. (About 5% of the dimethoxy derivative XLII was found as an impurity.) The yield of XLIII was 45%.

Dichlorocarbene from IX.—A solution of 33.0 g. (0.10 mole) of IX in 50 g. of cyclohexene was added dropwise to a stirred suspension of 10.8 g. (0.20 mole) of sodium methoxide in 32 g. of cyclohexene at 5–10° over a period of 2 hr. Stirring was continued for 3 hr. longer at 5–10° and for 18 hr. at room temperature. The black mixture then was filtered and the low-boiling material was distilled. Analysis of the distillate by g.l.c. showed that about 25% of the theoretical yield of chloroform was present. The less volatile material (9 g.) then was distilled at low pressure. The fraction boiling at 65–75° (8 mm.) weighed 2.0 g. and was found to contain about 50% 2,2-dichlorobicyclo-[4.1.0]heptane by mass spectrometry and g.l.c. The yield of this product was only 3–5%. The major product, *ca.* 4.5 g., b.p. 80–90° (5 mm.), m.p. 65–67°, was 2-methyl-4,6-dimethoxy-*s*-triazine (XLII).

N.m.r. Examination of Halogenation Products from 2-Ethyl-4,6-diphenyl-*s*-triazine.—2-Ethyl-4,6-diphenyl-*s*-triazine was mono- and dichlorinated and brominated as described by Reinhardt and Schiefer, and the four products were found to have the melting points reported.[5] The n.m.r. spectra of the two monohalides showed the expected quartet and doublet resonances for the methine and methyl groups, respectively, of the $-CHXCH_3$ structure. The n.m.r. spectra of the two dihalides showed single resonances due to the $-CX_2CH_3$ group rather than the complex pattern that would result from the $-CHXCH_2X$ structure. Thus there is no doubt that only α-halogenation of the ethyl group is significant.

Acknowledgment.—The authors wish to thank Dr. J. E. Lancaster and Mrs. M. R. Neglia for obtaining and interpreting the n.m.r. spectra which were of great assistance in this work. We are indebted to Mr. A. H. Struck and Mrs. R. H. Barritt for carrying out the mass spectrometric analyses. Valuable technical assistance was also provided by Mr. R. F. Phillips and Miss C. K. von Fényes.

Reactions of Benzaldehyde with *o*-Nitroaniline[1]

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When benzaldehyde and *o*-nitroaniline (I) are heated under reflux in toluene for varying lengths of time, not only is the anticipated product N-benzylidene-*o*-nitroaniline (II) formed but also N,N-benzylidenedi(*o*-nitroaniline) (III). Prolonged reaction time effects heterocyclization to give 1-hydroxy-2-phenylbenzimidazole (V) and 2-phenylbenzimidazole (IV). The structure of V was substantiated by its reduction to IV and by an alternate synthesis from N-benzyl-*o*-nitroaniline. Some intermediate conversions of interest were observed. The Schiff base II added *o*-nitroaniline to form III. Also, both II and III react with benzaldehyde to give V.

The reaction of aromatic aldehydes with aromatic amines usually proceeds without complication to form Schiff bases.[3] We have examined a case, however, where several subsequential reactions of interest occurred and found that control of experimental conditions was important in governing the outcome.

When *o*-nitroaniline was heated with an excess of benzaldehyde in toluene, the Schiff base, N-benzylidene-*o*-nitroaniline (II), was in fact obtained as the major product (see Chart A[4]); however, its separation and purification from the reaction mixture was made difficult by the presence of small amounts of N,N-benzylidenedi(*o*-nitroaniline) (III) and 1-hydroxy-2-phenylbenzimidazole (V).

N-Benzylidene-*o*-nitroaniline (II) on standing at room temperature will react with traces of moisture to form III (presumably the process involves initial hydrolysis to benzaldehyde and *o*-nitroaniline with subsequent addition of the latter to unchanged II). However, II is stable at 0° and may be stored at this temperature without evidence of transformation to III.

N,N-Benzylidenedi(*o*-nitroaniline) (III) was obtained as the sole product when benzaldehyde was heated with excess *o*-nitroaniline. Crude III displayed odd behavior on attempted purification. Recrystallization from several solvents gave materials of variable melting point. Although examination of these modi-

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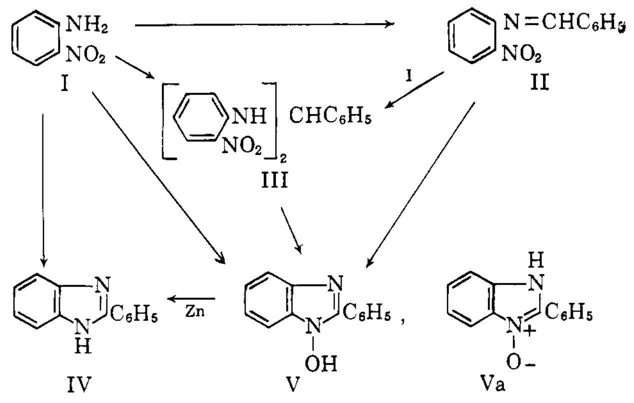
(1) Presented in part at the 1961 Northwest Regional Meeting of the American Chemical Society, Portland, Ore., June, 1961.

(2) In part abstracted from a thesis submitted by B. V. Ettling in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Washington State University, June, 1958. Public Health Service Research Fellow of the National Institute of Neurological Diseases and Blindness, 1956-1958.

(3) R. W. Layer, *Chem. Rev.*, **63**, 489 (1963).

(4) Unless otherwise indicated the reactant is benzaldehyde.

CHART A



fications was not complete, it was found that they all had the same bright orange-yellow color and quite similar infrared spectra but frequently varied in composition as indicated by elemental analysis. It finally was observed that, if the crude product was simply washed with several portions of cold toluene, a substance of constant melting point and purity was obtained. It appeared that the erratic melting point behavior might reflect heat lability of III. Acidic hydrolysis of III resulted in its decomposition to *o*-nitroaniline and benzaldehyde.

The ease of formation of III is consistent with the enhanced electron deficiency of the carbon atom of the carbon–nitrogen double bond of II which is influenced by the strongly electron-attracting *o*-nitro group. Thus, as expected, *o*-nitroaniline readily added to N-benzylidene-*o*-nitroaniline to yield III. There appears to be only one previous report of a stable compound of this type, N,N-trichloroethylidenedi(*o*-nitroaniline) which was obtained by condensing chloral with *o*-nitroaniline.[5]

A more convenient method for the preparation of II was developed.[6] When *o*-nitroaniline was heated with an equimolar quantity of N-benzylideneaniline under

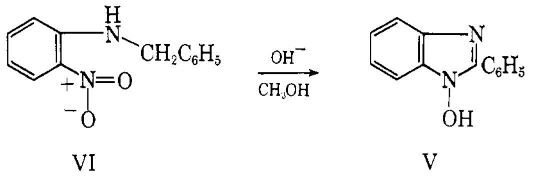
$$\underset{\text{I}}{o\text{-}O_2NC_6H_4NH_2} + C_6H_5N{=}CHC_6H_5 \rightleftharpoons \underset{\text{II}}{o\text{-}O_2NC_6H_4N{=}CHC_6H_5} + C_6H_5NH_2$$

reduced pressure (0.4 mm.), the free aniline which was displaced distilled, and the residue in the distilling flask was recrystallized from benzene–heptane. The infrared spectrum of the product showed as expected a strong band at 1629 cm.$^{-1}$ corresponding to the carbon–nitrogen double bond, whereas the spectrum of III did not have a band between 1800 and 1605 cm.$^{-1}$.

A somewhat higher temperature and a longer period of reflux promoted heterocyclization in the reaction of *o*-nitroaniline and benzaldehyde. Thus, when equimolar amounts were heated in xylene for seven days, 2-phenylbenzimidazole(IV) was isolated. When these reactants (1:2) were heated for three days in toluene, 1-hydroxy-2-phenylbenzimidazole(V) was obtained. The ultraviolet and infrared spectra of IV and V were quite similar, and V was converted to IV by heating with zinc dust. A comparison of infrared spectra also was made to the known 1-hydroxybenzimidazole[7] and again the agreement was quite good. 1-Hydroxy-2-phenylbenzimidazole (V) might also exist as an N-oxide structure (Va), a modification which has been favored recently for 1-hydroxybenzimidazole by Kew and Nelson.[8] Although these authors concluded that an N-oxide structure best explained the experimental results they describe, it would seem that an N-hydroxy structure would be just as valid.

We have determined n.m.r. spectra for 1-hydroxybenzimidazole and 1-hydroxy-2-phenylbenzimidazole-(V) in trifluoroacetic acid with a trace of tetramethylsilane added as an internal reference. If the N-oxide structure were the structure of choice, a broad peak due to the NH_2^+ ion probably would have been observed. Also, like phenylhydroxylamine, 1-hydroxy-2-phenylbenzimidazole(V) is photosensitive,[9] while the esterified (benzoyl) derivative is not. On the basis of these observations and considering that a noncharged structure would be more stable, it is felt that the N-hydroxy form V is the preferred tautomeric structure for benzimidazoles carrying the oxygen function in the 1-position.

To confirm the structure of V, an alternate method of formation was sought. Attempted peracid oxidation of 2-phenylbenzimidazole under a variety of conditions and concentrations failed. An attempt to cyclize *o*-nitrobenzanilide by the method of Niementowski[7] also was unsuccessful. Finally, the desired V was obtained by the base-catalyzed cyclization of N-benzyl-*o*-nitroaniline(VI). Base-catalyzed cyclizations involving condensation of nitro groups have been reported previously.[10]



Not only was it possible to form 1-hydroxy-2-phenylbenzimidazole (V) from *o*-nitroaniline (I), but it was obtained also by heating N-benzylidene-*o*-nitroaniline (II) or N,N-benzylidenedi(*o*-nitroaniline) (III), respectively, with benzaldehyde in toluene. Of course, this does not necessarily mean that II and III are intermediates in the formation of V.

Experimental[11]

N-Benzylidene-*o*-nitroaniline (II) from Benzaldehyde and *o*-Nitroaniline (I).—A solution of 6.90 g. (0.05 mole) of *o*-nitroaniline and 10.6 g. (0.10 mole) of benzaldehyde[12] in 10 ml. of dry

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[5] P. Grammaticakis, *Bull. soc. chim. France*, **17**, 158 (1950).

[6] This procedure was similar to that employed by Reddelien for preparing ketimines [G. Reddelien, *Ber.*, **54**, 3121 (1921)].

[7] S. Niementowski, *ibid.*, **43**, 3012 (1910).

[8] D. J. Kew and P. F. Nelson, *Australian J. Chem.*, **15**, 792 (1962).

[9] D. M. McQueen, U. S. Patent 2,426,894 (1947); *Chem. Abstr.*, **41**, 7290 (1947).

[10] (a) C. W. Muth, N. Abraham, M. L. Linfield, R. B. Wotring, and E. A. Pacofsky, *J. Org. Chem.*, **25**, 736 (1960); (b) G. Heller and G. Spielmeyer, *Ber.*, **58**, 834 (1925); (c) F. Arndt, *ibid.*, **46**, 3522 (1913).

[11] All melting points are corrected. The microanalytical work was performed by Galbraith Laboratories, Knoxville, Tenn., and by Weiler and Strauss Laboratories, Oxford, England. The infrared spectra were determined with a Perkin-Elmer Model 21 spectrophotometer. The samples were prepared as potassium bromide pellets (3 mg. of sample per 1 g. of potassium bromide).

[12] This was purified by washing commercial benzaldehyde with 10% sodium bicarbonate solution, drying over anhydrous potassium carbonate, and distilling under reduced pressure. It was stored in the absence of light and repurified every 2-3 months.

toluene was added under reflux for 32 hr. Most of the solvent was removed by distillation, and the residual solution was allowed to cool. A small amount of V (5%) crystallized and was separated. The remaining solvent was removed from the filtrate, and the oil was extracted with four 10-ml. portions of heptane to remove excess benzaldehyde. The oil was allowed to stand at −5°, and crude III crystallized and was removed by filtration, yielding 1.47 g. (16%), m.p. 105–109°. The filtrate again was extracted with 10 ml. of heptane, and the remaining oil was allowed to stand at −5°. Crystalline II was obtained after addition of a seed crystal and recrystallized from heptane–benzene, yielding 3.47 g. (31%), m.p. 76–77°.[13]

Anal. Calcd. for $C_{13}H_{10}N_2O_2$: C, 69.01; H, 4.45; N, 12.39. Found: C, 69.34; H, 4.52; N, 12.30.

The infrared spectrum showed a band assignable to C═N at 1629 (s) cm.$^{-1}$.

N,N-Benzylidenedi(*o*-nitroaniline) (III) from Benzaldehyde and *o*-Nitroaniline (I).—A solution of 6.90 g. (0.05 mole) of recrystallized *o*-nitroaniline and 3.20 g. (0.03 mole) of purified benzaldehyde in 10 ml. of dry toluene was heated under reflux for 9 hr., during which time 0.3 ml. of water was collected in a Dean–Stark trap. After the reaction mixture had been cooled in a refrigerator, the product was separated by filtration and washed with one 5-ml. portion of cold toluene, yielding 8.39 g. (92%), m.p. 68–72°. Recrystallization of this material from hot benzene led to material with variable melting points (94–118°) and which did not give satisfactory analyses. On the other hand, washing the product with five 5-ml. portions of toluene at room temperature yielded 3.10 g. (34%) of pure, bright orange-yellow crystals of N,N-benzylidenedi(*o*-nitroaniline), m.p. 94.5–95°.

Anal. Calcd. for $C_{19}H_{16}N_4O_4$: C, 62.63; H, 4.43; N, 15.38. Found: C, 62.69; H, 4.36; N, 15.21.

The infrared spectrum indicated bands assignable to N–H stretching vibrations (3345 cm.$^{-1}$, m) and NH deformation vibrations (1510 cm.$^{-1}$, s), characteristic of secondary amines.

Conversion of N-Benzylidene-*o*-nitroaniline (II) to N,N-Benzylidenedi(*o*-nitroaniline) (III).—In 5 ml. of heptane–benzene was placed 452 mg. (2.0 mmoles) of II, some of which, but not all, dissolved in the solvent. After standing for 1 week, the crystals had turned orange-yellow in color. This material was removed by filtration, yielding 353 mg. (97%), m.p. 114–116°. This substance proved to be identical with some of the material of variable melting point that was observed in the procedure above.

Addition of *o*-Nitroaniline to N-Benzylidene-*o*-nitroaniline (II).—A solution of 226 mg. (1.0 mmole) of II in 5 ml. of dry benzene was added to a solution of 138 mg. (1.0 mmole) of *o*-nitroaniline. The reaction mixture was heated at 80° for 1 hr., and then most of the solvent was removed by distillation under reduced pressure. The mixture was allowed to stand overnight in a freezer, during which time the product crystallized and was isolated by filtration, yielding 0.30 g. (83%), m.p. 100–101°. Washing with two 3-ml. portions of benzene at room temperature afforded a bright orange-yellow product, m.p. 95°, mixture melting point with the product obtained from the above procedure was 94.5–95°. The infrared spectra were also identical.

Anal. Calcd. for $C_{19}H_{16}N_4O_4$: C, 62.63; H, 4.43; N, 15.38. Found: C, 62.72; H, 4.65; N, 15.22.

Acidic Hydrolysis of N,N-Benzylidenedi(*o*-nitroaniline) (III).—A sample of 364 mg. (1.0 mmole) of III was added to aqueous ethanol and warmed gently. A solution of 250 mg. of 2,4-dinitrophenylhydrazine sulfate in ethanol–water was added, and the mixture was warmed at about 80° for 10 min. After the reaction mixture was cooled, a solid product was obtained by filtration. Recrystallization from benzene afforded orange benzaldehyde-2,4-dinitrophenylhydrazone, 283-mg. (96%) yield, m.p. 239–240°.

The filtrate from the recrystallization was concentrated and mixed with water. It and the filtrate from the hydrolysis were extracted with ether. The ether was removed from the combined extracts, and the residual *o*-nitroaniline (I) was recrystallized from heptane–benzene (5:1), yielding 229 mg. (83%), m.p. 70–71°; mixture melting point with authentic I was 70–71°.

N-Benzylidene-*o*-nitroaniline (II) from N-Benzylideneaniline and *o*-Nitroaniline (I).—In a 10-ml. flask assembled for distillation were introduced 4.14 g. (0.03 mole) of *o*-nitroaniline and 5.43 g. (0.03 mole) of N-benzylideneaniline. The reaction mixture was heated under reduced pressure (0.8 mm.) by means of an oil bath maintained at 150°. Over a period of 13 hr., 6 g. of an orange oil was distilled (b.p. 95–115°). The residue was placed in a freezer for 1 day during which time N-benzylidene-*o*-nitroaniline (II) crystallized; this was recrystallized twice from benzene–heptane (1:10) to give 3.85 g. (53%) of II, m.p. 76–78°; mixture melting point with material prepared by the alternate method described above was 76–77°.

2-Phenylbenzimidazole (IV).—A solution of 6.90 g. (0.05 mole) of *o*-nitroaniline and 5.30 g. (0.05 mole) of benzaldehyde in 50 ml. of xylene was heated under reflux until no more water was evolved (7 days). The reaction mixture was allowed to stand at room temperature, and the crystalline product which formed was isolated by filtration, yielding 2.50 g. (20%), m.p. 292–294°. Recrystallization of the crude product from ethanol–benzene (1:1) gave gray monoclinic prisms, m.p. 293–294°, lit.[14] m.p. 291°; mixture melting point with an authentic sample of IV[15] was 293–294°. The infrared spectrum indicated bands assignable to NH at 3100 (w) and aromatic C═C at 1560 (w) and 1450 (s) cm.$^{-1}$.

1-Hydroxy-2-phenylbenzimidazole (V).—A solution of 13.8 g. (0.10 mole) of *o*-nitroaniline and 21.2 g. (0.20 mole) of benzaldehyde in 20 ml. of dry toluene was heated under reflux for 3 days during which time 2.2 ml. of water was collected in a Dean–Stark trap. After the reaction mixture had been cooled, 18.9 g. of product was obtained by filtration. This crude product was purified by treatment with boiling ethanol, yielding 18.0 g. (86%), m.p. 220° dec., $\lambda_{\max}^{\mathrm{EtOH}}$ 298 mμ (ϵ 21,500).

Anal. Calcd. for $C_{13}H_{10}N_2O$: C, 74.27; H, 4.80; N, 13.33. Found: C, 74.47; H, 4.75; N, 13.50.

The infrared spectrum indicated bands assignable to OH at 3120 (w) and aromatic C═C at 1540 (w) and 1450 (s) cm.$^{-1}$.

1-Hydroxy-2-phenylbenzimidazole (V) by Cyclization of N-Benzyl-*o*-nitroaniline.—A solution of 4.56 g. (0.02 mole) of N-benzyl-*o*-nitroaniline[16] and 4.0 g. of sodium hydroxide in 80 ml. of dry methanol was heated under reflux on a steam bath for 5 hr. The reaction mixture then was concentrated to a volume of 30 ml. by distillation. The solution was neutralized with dilute hydrochloric acid, and the product was collected by filtration yielding 3.30 g. (79%), m.p. 220° dec. The mixture melting point with the product obtained from the reaction of *o*-nitroaniline and benzaldehyde gave a 15° depression, and the elemental analysis was inconsistent with that for V. However, brief treatment of this material with boiling water led to the formation of 1-hydroxy-2-phenylbenzimidazole (V), 2.30-g. (71%) yield, m.p. 220° dec.; mixture melting point with V obtained previously showed no depression (220° dec.), and the infrared spectra were identical.

Anal. Calcd. for $C_{13}H_{10}N_2O$: C, 74.27; H, 4.80; N, 13.33. Found: C, 74.09; H, 4.63; N, 13.02.

A **benzoyl derivative** was obtained from a mixture of 1.05 g. (5.0 mmoles) of 1-hydroxy-2-phenylbenzimidazole (V), 1.50 g. of benzoyl chloride, and 0.5 ml. of pyridine, which was heated at about 90° for 0.5 hr. and then allowed to cool. Water was added, and the resultant oil was removed by extraction with ether. The ether solution was shaken successively with dilute sodium bicarbonate solution and with hydrochloric acid. Evaporation of the ether followed by recrystallization of the residue from heptane gave colorless crystals, 1.13-g. (72%) yield, m.p. 116–118°.

Anal. Calcd. for $C_{20}H_{14}N_2O_2$: C, 76.42; H, 4.49; N, 8.91. Found: C, 76.67; H, 4.45; N, 9.01.

The infrared spectrum indicated an absorption band at 1766 cm.$^{-1}$ assignable to an ester C═O.

A **methyl derivative** was obtained from a solution of 210 mg. (1.0 mmole) of 1-hydroxy-2-phenylbenzimidazole (V) in methanol, to which an ether solution of diazomethane was added dropwise until rapid gas evolution ceased. The mixture was allowed to stand for 1 hr., and the solvent was removed by evaporation

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[13] C. K. Ingold and H. A. Piggott [*J. Chem. Soc.*, **121**, 2793 (1922)] reported the preparation of II by this method. Although the elemental analysis was consistent with II, it was orange-yellow, and the melting point reported was 118°, which is suggestive of III. Because II and III both occur in the same crude product and because II readily is converted to III on standing at room temperature, it is understood how a discrepancy could be encountered in reporting these results.

[14] H. Franzen, *Ber.*, **40**, 903 (1907).

[15] Prepared by the method of R. Walther and T. von Pulawski, *J prakt. Chem.*, [2]**59**, 249 (1899).

[16] Prepared in 80% yield by the method of M. S. Gibson [*J. Chem. Soc.*, 1076 (1956)].

The residue was recrystallized twice from diisopropyl ether to give 175 mg. (78%) of product, m.p. 102–104°.

Anal. Calcd. for $C_{14}H_{12}N_2O$: C, 74.98; H, 5.39; N, 12.49. Found: C, 74.79; H, 5.64; N, 12.31.

Zinc Dust Reduction of 1-Hydroxy-2-phenylbenzimidazole (V).—A mixture of 210 mg. (1.0 mmole) of V and 200 mg. (3.0 mg.-atoms) of zinc dust was heated at 240° for 2 hr. The mixture was allowed to cool and was extracted with warm ethanol. After the ethanol had been decanted, the residue was dissolved in dilute hydrochloric acid. The resulting solution was filtered, and the filtrate was made slightly basic. The basic filtrate then was extracted with three 15-ml. portions of warm chloroform. The chloroform was removed by distillation, and the residue was recrystallized from ethanol–benzene to yield 113 mg. of IV (58%), m.p. 292–294°, m.m.p. 293–294.5°.

Conversion of N-Benzylidene-*o*-nitroaniline (II) to 1-Hydroxy-2-phenylbenzimidazole (V).—A solution of 452 mg. (2.0 mmoles) of II and 212 mg. (2.0 mmoles) of benzaldehyde in 3 ml. of dry toluene was heated under reflux for 72 hr. The reaction mixture was allowed to stand in the freezer for 3 days, and the resulting crystalline precipitate was removed by filtration and purified by boiling toluene to give V in a 82-mg. yield (20%, m.p. 220° dec.). Identity was established by mixture melting point determination and infrared spectrum.

Conversion of N,N-Benzylidenedi(*o*-nitroaniline) (III) **to V.**—A solution of 364 mg. (1.0 mmole) of III and 318 mg. (3.0 mmoles) of benzaldehyde in 3 ml. of dry toluene was heated under reflux for 2 days. From the mixture was obtained 200 mg. of crude product which upon recrystallization from ethanol gave 117 mg. (56%) of V, m.p. 220° dec.

Acknowledgment.—We wish to express thanks to Varian Associates for assistance in determination and interpretation of n.m.r. spectra. This investigation was supported in part by a grant (G 1100) from the National Science Foundation.

Oxidation by Solids. III. Benzalanilines from N-Benzylanilines and Related Oxidations by Manganese Dioxide

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A variety of benzalanilines are readily obtained in excellent yield upon heating a suspension of manganese dioxide in a benzene solution of the corresponding N-benzylaniline in an apparatus equipped with a water trap. Close to theoretical yields of the by-product water collect at a rate which measures the rate of the oxidation. The effect of changes in structure of the reactants on the rate indicates that the process proceeds *via* free radicals. N-*t*-Alkyl benzylamines are also oxidized smoothly. Quinoline is obtained in good yield from 1,2,3,4-tetrahydroquinoline under the same conditions, and indole and acridine are readily prepared from 2,3-dihydroindole and acridane. The oxidation of a number of hydrazobenzenes to the azobenzenes proceeds rapidly in nearly quantitative yield, and, under modified conditions, azobenzenes are also obtained in good yield from a variety of anilines.

It has been found that, when a solution of an N-benzylaniline in benzene is heated under reflux with manganese dioxide in an apparatus equipped with a Bidwell–Sterling water trap, excellent yields of the corresponding benzalanilines and approximately theoretical yields of the by-product water are ordinarily obtained (Table I). These mild, anhydrous conditions prevent the further oxidation or hydrolysis of the product which often occurs when other methods of oxidation are used.[3,4]

$$p\text{-}RC_6H_4CH_2NHC_6H_4R'\text{-}p + MnO_2 \longrightarrow p\text{-}RC_6H_4CH = NC_6H_4R'\text{-}p + MnO + H_2O$$

A plot of the yield of water *vs.* time gives smooth curves of constantly decreasing slope which are closely reproducible and which show no tendency to cross one another as the reactant is varied. The times required for 50% of the theoretical yield of water to collect ($t_{50\%}$) are, therefore, valid measures of the relative reaction rates.

Data in the first and fourth sections of the table show that shifting a methoxyl group from the *para* to the *meta* to the *ortho* position or a methyl group from the *para* to the *ortho* position decreases the rate. The decrease in rate is reasonably ascribed to an increase in steric hindrance and as expected on this basis the shift of the methyl group has less effect than the shift of the larger methoxyl group.

It is of interest that dibenzylamine (fifth section) was oxidized at about the same rate as N-benzylaniline although only the latter compound gives a product in which the new double bond is conjugated with both aromatic rings. The oxidation also proceeded smoothly, although much more slowly, when the anilino ring of N-benzylaniline was replaced by tertiary alkyl groups.

No well-defined products were isolated when attempts were made to oxidize benzylamine, N-methylbenzylamine, N-isopropylbenzylamine, N-methylaniline, N-butylaniline, dibutylamine, or piperidine under the standard conditions. Apparently, unstable Schiff bases, which reacted further, were formed, since in all these cases water was collected in over 80% yield. Some of these amines have been oxidized by manganese dioxide under other conditions,[5,6] and, although in

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(1) From the Ph.D. thesis of T. P. McGovern, April, 1962.

(2) For the preceding paper in this series, see E. F. Pratt and S. P. Suskind, *J. Org. Chem.*, **28**, 638 (1963).

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