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o-Phenylenediamine is photo-oxidized to phenazine-2,3-diamine in ethanolic or aqueous hydrochloric acid solution. In acetic or propionic acid solutions it forms benzimidazole derivatives. *o*-Aminophenol in ethanol is photo-oxidized to 2-amino-3*H*-phenoxazin-3-one and two tetracyclic solvent addition products.

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o-Phenylenediamine has been oxidized to phenazine-2,3-diamine with various oxidants including silver oxide and lead dioxide [1], ferric chloride [2], copper perchlorate [3] and cobalt perchlorate [4]. *o*-Aminophenol has been oxidized to 2-amino-3*H*-phenoxazin-3-one (Questionmycin A) by cytochrome oxidase or lead dioxide [5]. However there are no reports of photochemical oxidations of *o*-phenylenediamine or *o*-aminophenol to heterocyclic compounds.

Results and Discussion.

When an ethanolic solution of *o*-phenylenediamine (**1**) was exposed to uv light (253.7 nm), while air was bubbled through it, it formed phenazine-2,3-diamine (**2**) (69%) as the only identified product. In the same way, when **1**, dissolved in dilute aqueous hydrochloric acid, was irradiated with aeration, the same product **2** was formed in 60% yield. In both experiments unreacted **1** was recovered and no other product was identified.

The photo-oxidation of **1** in alcoholic potassium hydroxide was performed. In this experiment the yield of **2** was reduced to 10% and the main product was identified as 2,2'-diaminoazobenzene (**3**).

A different reaction also occurred when a solution of **1** in acetic acid was photo-oxidized. The sole product identified was found to be 2-methylbenzimidazole (**4**) (73%). Similarly when the photo-oxidation of **1** was run in propionic acid 2-ethylbenzimidazole (**5**) was formed (62%).

The products **2**, **3**, **4** and **5** were identified by physical and spectral properties and had satisfactory elemental analyses.

Photo-oxidation of **1** → **2** can be suggested to involve hydrogen abstraction from **1** to give radicals **1a** and **1b**, which could combine leading to the formation of **2**.

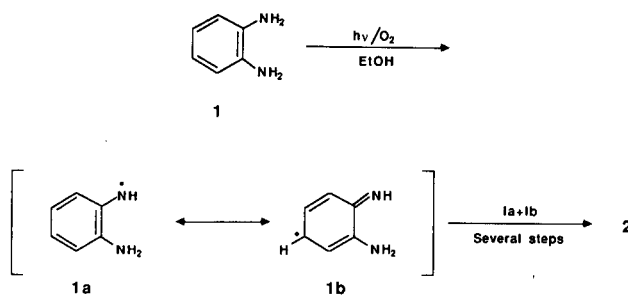


Fig.2

Condensation of **1** with carboxylic acids to form benzimidazoles is a process which normally occurs on refluxing the reactants with strong mineral acid for several hours [6]. The photochemical process reported here, with acetic and propionic acids, gave yields of the benzimidazoles **4** and **5** comparable to the conventional reaction. The conversion of **1** to **4** or **5** can be viewed as photo-oxidation of **1**, since three hydrogen atoms are removed from the diamine, however at this stage no mechanism can be postulated for the reaction process. Further work is under way to determine whether the process is a general one for *o*-diamines and carboxylic acids and to investigate the mechanism.

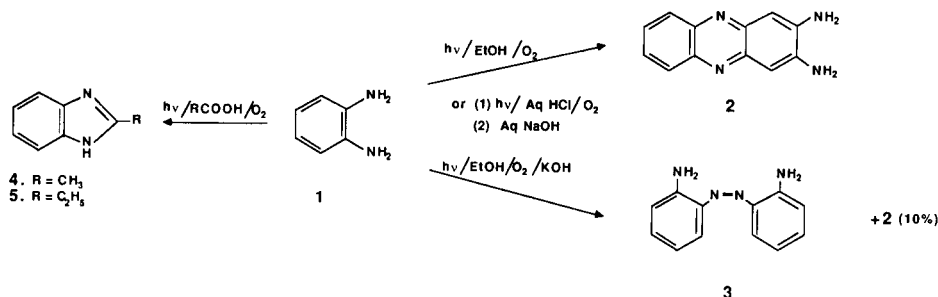


Fig.1

Photo-oxidation of *o*-aminophenol (**6**) was carried out in the same way and a tlc analysis of the reaction mixture revealed that three products had been formed. The mixture was resolved by column chromatography on silica gel and the three products were eluted in the following order.

2-Amino-3*H*-phenoxazin-3-one (Questionmycin A) (**7**) was obtained in 36% yield and was identified by spectroscopic means.

The second product **8** formed red crystals, mp 178-179°, and was shown by elemental analysis and mass spectrometry (M^+ , 310) to have a molecular formula $C_{18}H_{18}N_2O_3$. The ir spectrum showed the presence of NH (3325 cm^{-1}). The pmr spectrum indicated that **8** had an ethoxyl group, a methyl doublet at δ 1.41 and three other alicyclic ring hydrogens. It also showed the presence of five aromatic protons. The structure proposed is either 3-methyl-1-ethoxy-1,2,3,4-tetrahydro-3*H*-pyrido[3,2-*a*]-phenoxazin-3-one or the isomer 1-methyl-3-ethoxy-1,2,3,4-tetrahydro-3*H*-pyrido[3,2-*a*]phenoxazin-3-one, which can not be distinguished by the pmr spectrum.

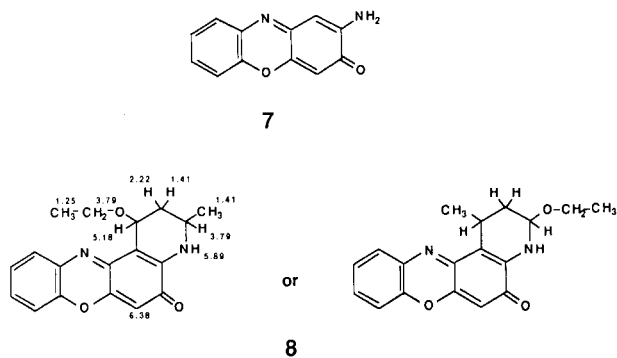


Fig. 3

The pmr signals observed are indicated on the structural formula of **8**. The 300 MHz spectrum showed that the CH_2 protons of the ethoxyl were not chemical shift equivalent, being close to a chiral carbon. When the CH_3 triplet at 1.25 was irradiated the CH_2 's were decoupled and formed an AB quartet. The spectral interpretation of other signals were confirmed by similar irradiations and decouplings.

The third product **9** formed dark red crystals, mp 187-190°, and was shown to have a molecular formula $C_{16}H_{14}N_2O_2$. Analysis of its ir and pmr spectra showed that its structure was closely related to **8** and it was identified as 1-methyl-1,2,3,4-tetrahydro-3*H*-pyrido[3,2-*a*]phenoxazin-3-one or the isomer 3-methyl-1,2,3,4-tetrahydro-3*H*-pyrido[3,2-*a*]phenoxazin-3-one.

The formation of **9** and **8** requires the photo-addition of a four carbon unit and a six carbon unit respectively to the original photoproduct **7**. It seems obvious that these are

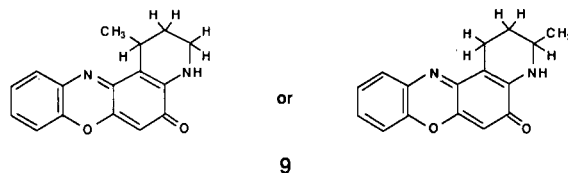


Fig. 4

derived from two and three molecules of the solvent ethanol respectively, by a mechanism which is presently not clear.

EXPERIMENTAL

Melting points were recorded on a Leitz hot stage microscope and are uncorrected. Elemental analyses were carried out by the Microanalytical Laboratory, University of New South Wales. Infrared spectra were recorded on a Pye Unicam SP-100 spectrometer and pmr spectra on a Jeol FX 100 spectrometer. Mass spectra were obtained from an AEI MS 12 spectrometer (70 ev). Starting materials were of high purity and solvents distilled before use.

Photo-oxidation of *o*-Phenylenediamine (**1**) in Ethanol.

o-Phenylenediamine (1.08 g, 0.01 mole) in 95% ethanol (300 ml) was placed in a quartz flask and exposed to uv light (253.7 nm) for 3 days. During the exposure air was gently bubbled through the solution. Evaporation of solvent *in vacuo* left a brown residue separated by chromatography on silica gel [light petroleum:ethyl acetate (7:3)] to give the product 2,3-diaminophenazine (**2**) (0.72 g, 69%) mp 265-266° (lit [7] 264°).

Photo-oxidation of *o*-Phenylenediamine (**1**) in Dilute Hydrochloric Acid.

o-Phenylenediamine (1.08 g, 0.01 mole) in 1*M* aqueous hydrochloric acid (300 ml), was irradiated with aeration as described above. The pH of the reaction mixture was then adjusted to 10 by addition of sodium hydroxide solution and extracted with ethyl acetate (4 x 100 ml). The extract was dried, concentrated and chromatographed as previously described to yield (**2**) (0.63 g, 60%) with properties identical with the previous product.

Photo-oxidation of *o*-Phenylenediamine (**1**) in Acetic Acid.

o-Phenylenediamine (1.08 g, 0.01 mole) in glacial acid (100 ml), was irradiated with aeration in the same way. The solvent was evaporated *in vacuo* to give a brown solid which was dissolved in 200 ml of hot water, charcoaled, and the solution slowly evaporated until the product crystallized. 2-Methylbenzimidazole (**3**) was obtained as colourless crystals (0.9 g, 73%) mp 176° (lit [8] mp 178°).

Photo-oxidation of *o*-Phenylenediamine (**1**) in Propionic Acid.

o-Phenylenediamine (1.08 g, 0.01 mole) in propionic acid (100 ml) was irradiated with aeration in the same way. The solvent was evaporated *in vacuo* to give a brown solid, which was dissolved in boiling water and charcoaled. On cooling, the product 2-ethylbenzimidazole was obtained as colourless crystals (0.9 g, 62%) mp 175° (lit [8] mp 177°).

Photo-oxidation of *o*-Phenylenediamine (**1**) in Alcoholic Potassium Hydroxide.

o-Phenylenediamine (1.08 g, 0.01 mole) in ethanol (300 ml) containing potassium hydroxide (2 g) was irradiated with aeration for 3 days. The reaction mixture was evaporated to dryness (rotary) and the residue was dispersed in water (50 ml) and extracted with ethyl acetate (6 x 50 ml). The solvent layer was concentrated and chromatographed on silica gel to give 2,3-diaminoazobenzene (**4**) (0.64 g, 60%), red plates mp 135°, undepressed mp when mixed with an authentic sample. 2,3-Diaminophenazine (**2**) was also obtained in 10% yield.

Photo-oxidation of *o*-Aminophenol (**5**) in Ethanol.

o-Aminophenol (1.09 g, 0.01 mole) in ethanol (300 ml) was irradiated with uv light with aeration for 3 days. The solvent was evaporated to give a brown residue which was separated by silica gel column chromatography. Elution with light petrol (60-80 bp):ethyl acetate mixtures gave the following:

2-Amino-3*H*-phenoxazin-3-one (**6**) was obtained in the form of dark purple crystals, mp 250-252° (lit [9] mp 250°) (0.38 g, 36%).

A red crystalline compound (**7**) mp 178-179° (0.28 g) was obtained; ms: m/e 310 (M⁺), 266; ir (potassium bromide): 640, 670, 720, 725, 745, 760, 785, 850, 900, 980, 1040, 1080, 1100, 1180, 1220, 1280, 1310, 1320, 1340, 1360, 1490, 1520, 1580, 1620, 1640, 2725, 2950, 3020, 3325 cm⁻¹; pmr (deuteriochloroform): δ 1.25 (t, 3H, CH₃ CH₂), 1.41 (d + m, 4H, CH₃ CH and C2 CH), 2.22 (m, 1H, C2 CH), 3.79 (m, 3H, CH₂ CH₃ and H3), 5.18 (dd, 1H, H1), 5.84 (s, 1H, NH), 6.32 (s, 1H, H6), 7.27-7.78 (m, 4H, H8, H9, H10, H11).

Anal. Calcd. for C₁₈H₁₈N₂O₃: C, 69.7; H, 5.8; N, 9.0. Found: C, 69.9; H, 5.6; N, 8.7.

A dark red crystalline compound **8** mp 187-190° (0.10 g) was obtained; ms: m/e 266; ir (potassium bromide): 730, 760, 830, 840, 900, 970, 1040, 1120, 1150, 1190, 1200, 1220, 1270, 1280, 1310, 1340, 1350, 1480, 1520, 1580, 1620, 1640, 2780, 2950, 3040, 3340 cm⁻¹; pmr (deuteriochloroform): δ 1.33 (d, 3H, CH₃ CH), 1.69 (m, 1H, C2 CH), 2.04 (m, 1H, C2 CH), 2.93 (m, 2H, C1 CH₂), 3.60 (m, 1H, CH₃CH), 5.66 (s, 1H, NH), 6.31 (s, 1H, H6), 7.28-7.81 (m, 4H, H9, H10, H11, H12).

Anal. Calcd. for C₁₆H₁₄N₂O₂: C, 72.2; H, 5.3; N, 10.5. Found: C, 72.4; H, 5.3; N, 10.4.

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