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APPLICATION OF 1,2-DIKETONES IN THE SYNTHESIS OF PHENAZINE OXIDES

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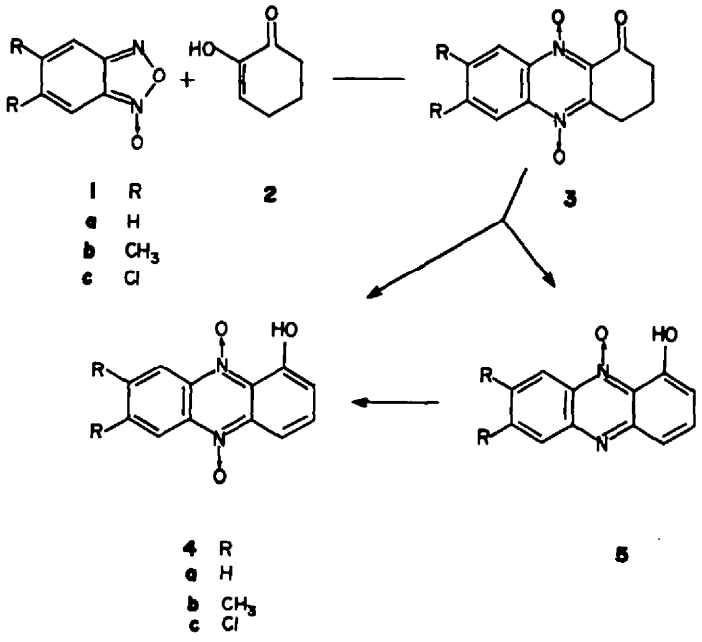
Abstract—Simple routes to phenazine oxides via 1,2-diketones are reported.

This paper describes the application of some 1,2-diketones for the preparation of phenazine oxides of a substitution pattern not possible to obtain by the recently reported route via phenols and benzofurazan oxide.[1] The present method comprises two lines of approach: in one, the readily enolizable cyclohexane - 1,2 - dione is allowed to react with benzofurazan oxide in the presence of diethyl amine to give phenazine oxides possessing OH substituents at position 1; in another, 1,2-diketones are treated with anions derived from 2,3 - dimethylquinoxaline - di - N - oxides to give phenazine oxides substituted at (phenazine) positions 2 and 3.

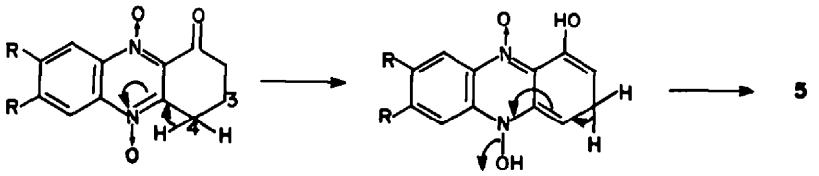
I. *Reaction of cyclohexane - 1,2 - dione with benzofurazan oxide*

Despite its versatility, the route to phenazine - di - N - oxides from phenols and benzofurazan oxide[1] is not practicable for compounds of the substitution type defined by 1 - hydroxyphenazine - 5,10 - dioxide (**4a**). This compound, along with myxin (1 - hydroxy - 6 - methoxyphenazine - 5,10 - dioxide), iodinin (1,6 - dihydroxyphenazine - 5,10 - dioxide), and other analogs are of particular interest because they possess enhanced biological activity.[2]

Our expectation at the outset of this study was that, by analogy to other enolate anions,[3] cyclohexane - 1,2 - dione[4] (**2**) would react with benzofurazan oxides (**1**) to give intermediate **3**, which would then undergo dehydrogenation (analogous to that of the intermediate in the reaction between phenols and benzofurazan oxide[1]) to give the desired 1 - hydroxyphenazine - 5,10 - dioxides (**4**, Scheme 1). The experimental results did not fully meet the original expectations: when benzofurazan oxide was heated with 1,2-cyclohexanedione in diethylamine, a mixture was obtained containing not only the desired product (**4**) but also monoxide(s) of 1 - hydroxypehnazine (**5**), the latter probably arising by a base-induced tautomeric shift in **3** followed by dehydration (Scheme 2). Although two isomeric monoxides may arise depending on whether a methylene hydrogen at C-3 or C-4 is involved in the tautomeric shift of **3**, TLC with different solvent systems showed the monoxide to be homogeneous (tentatively formulated as **5**, on the basis of the enhanced acidity of the methylene hydrogens alpha to the nitrone function of **3**). In order to improve the yield of the dioxides **4**, the mixture obtained in Scheme 1, without further separation, was treated with 3-chloroperbenzoic acid in benzene. This procedure not only



Scheme 1.



3 **5**

Scheme 2.

gave the desired dioxides in good yield (**4a**, 56%; **4b**, 59%; **4c**, 36%) but also facilitated considerably their isolation.

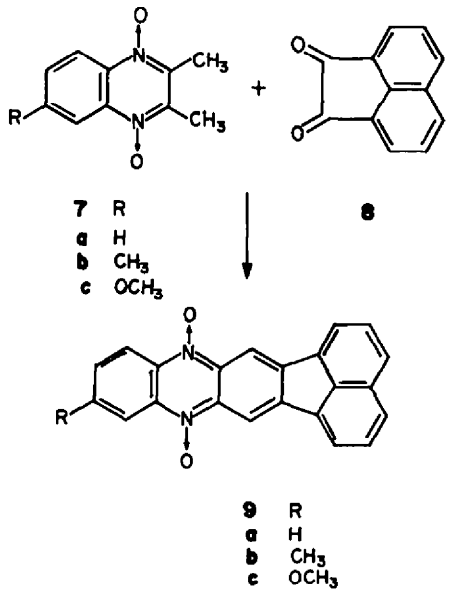
All the 1 - hydroxyphenazine - 5,10 - dioxides described here are intensely colored crystalline solids (from MeOH–$CHCl_3$: **4a** and **4b** dark red, **4c** dark golden-purple), displaying a broad band at 3400 cm^{-1} and a strong band at 1340 cm^{-1}. Deoxygenation by sodium dithionite to the corresponding 1-hydroxyphenazines (all yellow from EtOH–H_2O) was attended with disappearance of the 1340 cm^{-1} in the IR, and with a hypsochromic shift (20–30 nm) of the short-wavelength band in the UV (288–265 for **4a**, 294–265 for **4b**, 304–275 for **4c**).

II. *Condensation of* 2,3 - *dimethylquinoxaline* - 1,4 - *dioxides with* 1,2-*diketones*

The nitrone group (**6**) markedly resembles the CO group in facilitating the removal of a proton from an alpha C atom.[5] Since the N-oxide functions of quinoxaline - di - N - oxides may be regarded as the combination of two nitrone groups, Me hydrogens at positions 2 and 3 in compounds such as **7** are expected to

6

show enhanced acidity. Advantage of this acidity was taken in the extremely rapid condensation of **7** with acenaphthenequinone (**8**) in methanolic potassium hydroxide to give substituted phenazine - di - N - oxides in very good yields (**9a**, 90%; **9b**, 70%; **9c**, 75%, Scheme 3). These products showed IR absorption bands at cm^{-1} 1330–1340 (N→O stretching), 830 and 770–780.



7 R
a H
b CH_3
c OCH_3

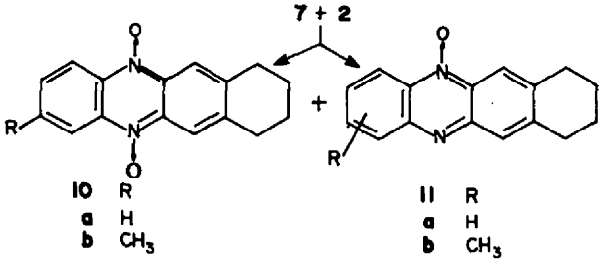
8

9 R
a H
b CH_3
c OCH_3

Scheme 3.

The dioxides **7** reacted with 1,2-cyclohexanedione (**2**) in methanolic potassium hydroxide as rapidly as they did with **8**, but in this case the products were mixtures of the tetrahydrobenzo[b]phenazine - di - N - oxides (**10**) and the corresponding monoxides (**11**). The products (separated by thick-layer chromatography) were obtained in low yields (Scheme 4: **10a**, 17%; **11a**, 6%; **10b**, 7%; **11b**, 3%). They all showed bands at cm^{-1} 2940 (methylene stretching), 1340–1350 and 640–900. As expected, oxidation of **11a** by 3-chloroperbenzoic acid gave **10a**.

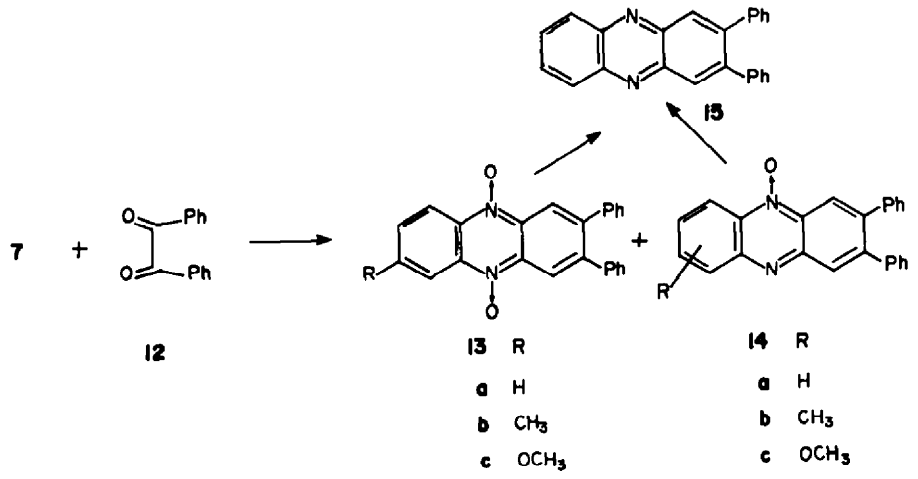
Whereas the reactions outlined in Schemes 3 and 4 proceeded remarkably fast, the base-induced condensation of **7** with benzil (**12**) was so sluggish as to require 2–3 days for completion. The products were mixtures of 2,3 - diphenylphenazine - di - N - oxides (**13**) and the



10 R
a H
b CH_3

11 R
a H
b CH_3

Scheme 4.



Scheme 5.

corresponding monoxides (**14**). Separation was effected by thick-layer chromatography, and yields were low (Scheme 5: **13a**, 14%; **14a**, 6%; **13b**, 5%; **14b**, 10%; **13c**, 5%; **14c**, 3%). The products showed bands at cm^{-1} 1335–1345, 890–900, 770–780 and 700. The NMR spectra of **13a** and **14a** are noteworthy. In the more symmetrical di - N - oxide **13a** the three different kinds of protons were clearly resolved (δ-values): the deshielded protons at C_1 and C_4 appeared as a singlet at 8.3, and the almost isochronous protons at C_6 and C_9 gave a multiplet centered at 8.3; the protons at C_7 and C_8 gave a multiplet centered at 7.4, and the ten protons of the two phenyl groups at C_2 and C_3 gave a singlet at 6.9. The less symmetrical monoxide **14a** showed four kinds of protons: a singlet and a multiplet at 8.3 (protons at C_1 and C_9), a singlet and a multiplet at 7.8 (protons at C_4 and C_6),.a multiplet at 7.4 (protons at C_7 and C_8) and a singlet at 6.9 (10 protons). Oxidation of **14a** with 3-chloroperbenzoic acid gave **13a** and deoxygenation of either **13a** or **14a** by sodium dithionite gave 2,3-diphenylphenazine (**15**).

The formation of the monoxides **11** and **14** merits some explanation. We believe that these products arise by the carbanion induced deoxygenation depicted in Scheme 6. In support of this postulate is the observation that **13a** is partially converted into **14a** after standing for two days at room temperature in methanolic potassium hydroxide containing **7**, whereas it is recovered unchanged under the same conditions, but in the absence of **7**. Failure to isolate product **16** is not surprising in view of its expected lability in base.[6]

Condensations of **7** with phenylglyoxal, isatin, biacetyl and diethyl oxalate were also attempted, but the reactions either failed or yielded intractable mixtures.

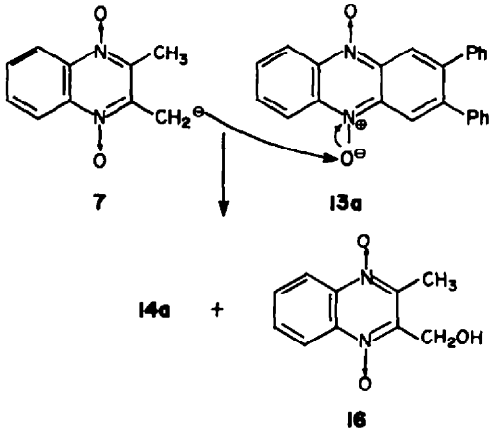
Closely related to the reactions described here is the condensation of 2 - methylquinoxaline - di - N - oxide (**17**) in base with benzaldehyde to give the 2-styryl derivative **18** in good yield (Scheme 7, 65%). The product showed bands at cm^{-1} 1625, 1370–1375, 970 (*trans* double bond), and 690.

EXPERIMENTAL

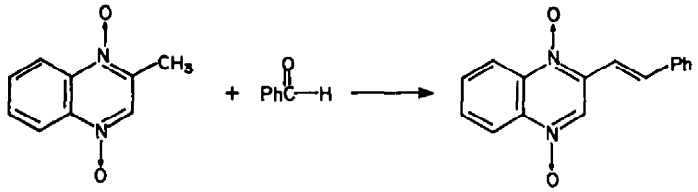
M.ps were determined on a Fisher–Johns apparatus and were uncorrected. IR spectra (KBr) were taken on a Perkin–Elmer 257 Spectrometer. ^1H NMR (δ) were run in $CDCl_3$ on a Varian A60-D Spectrometer. Elemental analyses were performed by F. Pascher, Bonn, Germany. Silica gel GF_{254} (Merck) was used in TLC. All the benzofurazan oxides were prepared by a slight modification of Mallory's[7] method where commerical sodium hypochlorite solution (800 ml per 0.3 mole of the specific *o*-nitroaniline) was substituted for chlorine.

General procedure A

The reaction of benzofurazan oxide with 1,2-cyclohexanedione. A soln of the specific benzofurazin oxide in diethylamine or triethylamine was added dropwise to 1,2-cyclohexanedione in a 250 ml, 3-necked round-bottomed flask equip-



Scheme 6.



17 18

Scheme 7.

ped with a mechanical stirrer. After the addition of the benzofurazan oxide soln was completed, the mixture was stirred for a specific length of time. The mixture was diluted with crushed ice and acidified with AcOH. The brown-red solid was collected, washed with water and dried. TLC showed the presence of red and olive green products.

General procedure B

The oxidation with 3-chloroperbenzoic acid. The crude product from procedure A was dissolved in benzene and a warm benzene soln of 3-chloroperbenzoic acid was added to it. The mixture was either left to stand at room temp. or refluxed for some time. The soln was extracted with a 10% Na_2SO_3 aq followed by a 10% $NaHCO_3$ aq. Evaporation of the dried benzene soln gave a dark red solid which was treated with a 10% NaOH aq. The resulting blue soln was acidified with AcOH to afford the product as a bright red solid. Recrystallization from MeOH–$CHCl_3$ or separation by column chromatography (silica gel) yielded the pure product.

1 - *Hydroxyphenazine* - 5,10 - *dioxide* (**4a**)

Benzofurazan oxide (10.2 g, 0.07 mole), 1,2-cyclohexanedione (4.2 g, 0.035 mole), DEA (100 ml), 30 min in ice-bath, 1 hr at room temp. The crude product (7.32 g) was oxidized with 3-chloroperbenzoic acid (7.32 g) for 12 hr at room temp. Dark red needles, 4.5 g, 56%, m.p. 184–185 (lit.[8] 189–190°). TLC in different solvents confirmed the homogeneity of the product. IR ν_{max} 3400, 3100, 1590, 1550, 1470, 1400, 1380, 1345, 1320, 1300, 1260, 1245, 1095, 1060, 1040, 880, 835, 800, 770, 750, 655 cm^{-1}. ^1H NMR 7.0 (m, 2H), 7.7 (m, 4H), 8.3 (m, 2H). (Found: C, 63.67; H, 3.67; N, 12.18. Calc. for $C_{12}H_8N_2O_3$: C, 63.16; H, 3.53; N, 12.28%).

7,8 - *Dimethyl* - 1 - *hydroxyphenazine* - 5,10 - *dioxide* (**4b**). 5,6-Dimethylbenzofurazan oxide (5.3 g, 0.032 mole), DEA (100 ml), 1,2-cyclohexanedione (1.9 g, 0.016 mole), 2 hr at room temp. TLC indicated red and olive green products. Crude product (2.5 g), 3-chlorperbenzoic acid (4.0 g, 0.02 mole) in benzene, reflux 24 hr. Separation by silica gel column chromatography (pet. ether–benzene, 3:7). Dark red needles m.p. 180–181° dec. 1.2 g, 59%. IR ν_{max} 3400, 3100, 2900, 1620, 1550, 1500, 1475, 1410, 1385, 1340, 1280, 1265, 1180, 1135, 1100, 1060, 1040, 1010, 915, 805, 750, 680 cm^{-1}. ^1H NMR 2.4 (s, 6H), 7.5 (m, 6H). (Found: C, 65.14; H, 4.73; N, 11.03. Calc. for $C_{14}H_{12}N_2O_3$: C, 65.62; H, 4.72; N, 10.92%).

7,8 - *Dichloro* - 1 - *hydroxyphenazine* - 5,10 - *dioxide* (**4c**). 5,6-Dichlorobenzofurazan oxide (12.0 g, 0.06 mole) TEA (200 ml), 1,2-cyclohexanedione (3.66 g, 0.03 mole), 10 hr in ice-bath. TLC indicated purple and olive green products which were isolated by thick layer chromatography. Crude products (2.0 g), 3-chloroperbenzoic acid (4.0 g, 0.02 mole) in benzene, reflux 30 min. Dark purple solid, m.p. 208–209°, 1.6 g, 36%. IR ν_{max} 3400, 3085, 1620, 1580, 1540, 1490, 1450, 1420, 1395, 1355, 1340, 1240, 1225, 1205, 1180, 1140, 1110, 1095, 1060, 1040, 910, 900, 830, 785, 735, 720, 665, 635 cm^{-1}. ^1H NMR 7.5 (m). (Found: C, 48.02; H, 1.93; N, 9.22; Cl, 23.43. Calc. for $C_{12}H_6N_2O_3Cl_2$: C, 48.48; H, 2.02; N, 9.42; Cl, 23.90%).

1-*Hydroxyphenazine.* 1 - Hydroxyphenazine - 5,10 - dioxide (1.0 g, 0.004 mole) in 5% NaOH aq (50 ml) was treated with a 40% $Na_2S_2O_4$ aq (10 ml) added over 30 min. Acidification with AcOH gave a brown-yellow solid which upon recrystallization from EtOH-water gave fluffy yellow needles of 1-hydroxyphenazine, 0.3 g, 80%, m.p. 157–159° (lit.[9] 157–158°). 1-Acetoxyphenazine (acetic anhydride : pyridine) melted at 120–121° (lit.[9] 123°).

7,8 - *Dimethyl* - 1 - *hydroxyphenazine.* A soln of $Na_2S_2O_4$ aq (0.5 g, 10 ml) was added dropwise (1 hr) to a hot soln of 7,8 - dimethyl - 1 - hydroxyphenazine - 5,10 - dioxide (0.1 g, 3×10^{-4} mole) in 1,2-dimethoxyethane (40 ml) at 80°. The soln was diluted with water and the yellow solid was recrystallized from EtOH-water, 0.05 g, 82%, m.p. 209–210° dec. IR ν_{max} 3400, 2990, 2910, 1640, 1570, 1515, 1480, 1450, 1370, 1360, 1240, 1140, 1090, 1035, 1010, 875, 840, 790, 755, 720 cm^{-1}. ^1H NMR 2.4 (s, 6H), 7.5 (m, 6H). (Found: C, 74.36; H, 5.26; N, 12.56. Calc. for $C_{14}H_{12}N_2O$: C, 74.99; H, 5.54; N, 12.49%).

7,8 - *Dichloro* - 1 - *hydroxyphenazine.* The procedure for the reduction of 7,8 - dimethyl - 1 - hydroxyphenazine - 5,10 - dioxide was followed. 7,8 - Dichloro - 1 - hydroxyphenazine - 5,10 - dioxide (0.1 g, 3×10^{-4} mole) yielded 0.051 g, 65% of the yellow product m.p. 113–115°. IR ν_{max} 3400, 3040, 2965, 1630, 1500, 1460, 1450, 1420, 1370, 1350, 1220, 1100, 1080, 990, 880, 830, 755, 740 cm^{-1}. ^1H NMR 7.3.

General procedure C

The reaction of 2,3 - dimethylquinoxaline - 1,4 - dioxides with 1,2-diketones. The specific 2,3 - dimethylquinoxaline - 1,4 - dioxide (**7**) and the specific 1,2 - diketone (**8**, **2** or **12**) were dissolved in warm MeOH. A 10% methanolic KOH soln was added and the mixture was left to stand at room temp. for some time. The product precipitated out and was collected. Mixtures of dioxides and monoxides were separated by thick layer chromatography on silica gel and elution with benzene–MeOH (1% MeOH).

Acenaphtho[1,2 - b]*phenazine* - 5,10 - *dioxide* (**9a**). 2,3 - Dimethylquinoxaline - 1,4 - dioxide (0.5 g, 2.5 mmole), acenaphthenequinone (0.46 g, 2.5 mmole), immediate product, 0.7 g, second crop, 0.12 g, 1 day, 90%, m.p. 255° (from AcOH). IR ν_{max} 1470, 1450, 1340, 1320, 1095, 830, 770, 735, 680 cm^{-1}. (Found: C, 78.61; H, 3.77; N, 8.43. Calc. for $C_{22}H_{12}O_2N_2$: C, 78.56; H, 3.60; N, 8.33%).

10 - *Methxyacenaphtho*[1,2 - b]*phenazine* - 5,10 - *dioxide* (**9b**). 2,3,6 - Trimethylquinoxaline - 1,4 - dioxide (0.25 g, 1.3 mmole). 1 day, 0.32 g, 70%, the product was digested in hot MeOH, m.p. 240° dec. IR ν_{max} 1445, 1330, 1230, 1085, 900, 830, 780, 720 cm^{-1}. (Found: C, 78.25; H, 4.07; N, 8.24. Calc. for $C_{23}H_{14}N_2O_2$: C, 78.84; H, 4.03; N, 8.00%).

10 - *Methoylacenaphtho*[1,2 - b]*phenazine* - 5,10 - *dioxide* (**9c**). 2,3 - Dimethyl - 6 - methoxyquinoxaline - 1,4 - dioxide (0.28 g, 1.25 mmole), acenaphthenequinone (0.25 g, 1.3 mmole). 1 day,; 0.35 g, 75%, m.p. 245–247°. IR ν_{max} 1610, 1480, 1450, 1410, 1335, 1250, 1210, 1080, 1020, 880, 825, 775, 730 cm^{-1}. (Found: C, 73.98; H, 4.04; N, 7.69. Calc. for $C_{23}H_{14}N_2O_3$: C, 75.40; H, 3.85; N, 7.65%).

Tetrahydrobenzo[b]*phenazine* - 5,10 - *dioxide* (**10a**) *and tetrahydrobenzo*[b]*phenazine* - *mono* - N - *oxide* (**11a**). 2,3 - Dimethylquinoxaline - 1,4 - dioxide (0.95 g, 5 mmole) in water (10 ml), 1,2-cyclohexanedione (0.54 g, 5 mmole) in water (60 ml). Two days, products were separated by TLC, **10a**, 0.2 g, 17%, m.p. 193–195° (MeOH). IR ν_{max} 2930, 1620, 1445, 1340, 1300, 1180, 1125, 1080, 920, 875, 770, 760, 735, 670 cm^{-1}. (Found: C, 72.02; H, 5.18; N, 10.62. Calc. for $C_{16}H_{14}N_2O_2$: C, 72.16; H, 5.30; N, 10.52%). **11a**, 0.07 g, 6%, m.p. 181–183°. IR ν_{max} 2940, 1560, 1500, 1470, 1440, 1425, 1400, 1340, 1270, 1100, 920, 860, 765 cm^{-1}. (Found: C, 76.52; H, 5.58; N, 11.17. Calc. for $C_{16}H_{14}N_2O$: C, 76.78; H, 5.64; N, 11.19%).

8 - *Methyltetrahydrobenzo*[b]*phenazine* - 5,10 - *dioxide* (**10b**) *and* 8(9) - *methyltetrahydrobenzo*[b]*phenazine* - *mono* - N - *oxide* (**11b**). 2,3,6 - Trimethylquinoxaline - 1,4 - dioxide (1.1 g, 5 mmole)

in water (50 ml), 1,2-cyclohexanedione (0.6 g, 5 mmole) in MeOH (20 ml). Two days, products were separated by TLC, **11a**, 0.1 g, 7%, m.p. 183–185°. IR ν_{max} 2940, 1615, 1450, 1415, 1340, 1320, 1180, 1120, 1075, 925, 870, 815, 720 cm^{-1}. (Found: C, 72.75; H, 5.83; N, 10.04. Calc. for $C_{17}H_{16}N_2O_2$: C, 72.84; H. 5.75; N, 9.99%). **11b**, 0.036 g, 3%. IR ν_{max} 2940, 1630, 1550, 1500, 1440, 1400, 1350, 1330, 1270, 920, 870, 820, 700 cm^{-1}.

2,3 - *Diphenylphenazine* - 5,10 - *dioxide* (**13a**) *and* 2,3 - *diphenylphenazine* - *mono* - N - *oxide* (**14a**). 2,3 - Dimethylquinoxaline - 1,4 - dioxide (3.8 g, 20 mmole) in MeOH (40 ml), benzil (4.2 g, 20 mmole) in MeOH (60 ml). Three days, products were separated by TLC. **13a**, 1 g, 14%, m.p. 196–198°. IR ν_{max} 3050, 1430, 1340, 1320, 1230, 1100, 900, 780, 770, 635 cm^{-1}. ^1H NMR 8.3 (s, m, 4H), 7.4 (m, 2H), 6.9 (s, 10H). (Found: C, 79.01; H, 4.33; N, 7.80. Calc. for $C_{24}H_{16}O_2N_2$: C, 79.10; H, 4.43; N, 7.69%). **14a**, 0.43 g, 6%, m.p. 177–179°, IR ν_{max} 3050, 1550, 1500, 1440, 1430, 1390, 1350, 1240, 890, 780, 765, 700 cm^{-1}. ^1H NMR 8.3 (s, m, 2H), 7.8 (s, m, 2H), 7.4 (m, 2H), 6.9 (s, 10H). (Found: C, 82.75; H, 4.57; N, 8.05. Calc. for $C_{24}H_{16}ON_2$: C, 82.74; H, 4.63; N, 8.04%).

7 - *Methyl* - 2,3 - *diphenylphenazine* - 5,10 - *dioxide* (**13b**) *and* 7(8) - *methyl* - 2,3 - *diphenylphenazine* - *mono* - N - oxide (**14b**). 2,3,6 - Trimethylquinoxaline - 1,4 - dioxide (4.1 g, 20 mmole), benzil (4.2 g, 20 mmole) in warm MeOH (80 ml). Two days, the solvent was evaporated and the acidified (HCl) residue was extracted with $CHCl_3$, the products were separated by column chromatography on neutral alumina (benzene) followed by TLC. **13b**, 0.4 g, 5%, m.p. 210–212°. IR ν_{max} 3040, 1640, 1440, 1420, 1335, 1230, 1200, 1090, 890, 780, 760, 700, 650 cm^{-1}. (Found: C, 79.20; H, 4.65; N, 7.71. Calc. for $C_{25}H_{18}N_2O_2$: C, 79.35; H, 4.79; N, 7.40%). **14b**, 0.7 g, 10%, m.p. 170–172°. IR ν_{max} 3050, 1625, 1600, 1550, 1490, 1440, 1420, 1380, 1345, 1240, 890, 875, 815, 780, 770, 700 cm^{-1}. (Found: C, 82.60; H. 4.94; N, 7.90. Calc. for $C_{25}H_{18}N_2O$: C, 82.85; H, 5.01; N, 7.73%).

7 - *Methoxy* - 2,3 - *diphenylphenazine* - 5,10 - *dioxide* (**13c**) *and* 7(8) - *methoxy* - 2,3 - *diphenylphenazine* - *mono* - N - *oxide* (**14c**). 2,3 - Dimethyl - 6 - methoxyquinoxaline - 1,4 - dioxide (3.3 g, 15 mmole), benzil (3.2 g, 15 mmole) in warm MeOH (170 ml). The same procedure for **13b**, **14b** was followed. **13c**, 0.3 g, 5%, m.p. 213–215°. IR ν_{max} 3050, 1620, 1600, 1465, 1425, 1340, 1240, 1230, 1210, 1085, 1020, 900, 840, 780, 765, 700, 650 cm^{-1}. (Found: C, 75.89; H, 4.56; N, 7.26. Calc. for $C_{25}H_{18}N_2O_3$: C, 76.13; H, 4.60; N,7.10%). **14b**, 0.15 g, 3%, m.p. 178–180°. IR ν_{max} 3050, 1625, 1600, 1560, 1465, 1440, 1425, 1400, 1350, 1300, 1235, 1200, 1100, 1020, 895, 840, 830, 785, 770, 705 cm^{-1}. (Found: C, 78.15; H, 4.71; N, 7.30. Calc. for $C_{25}H_{18}N_2O_2$: C, 79.35; H, 4.79; N, 7.40%).

Oxidation of 2,3 - *diphenylphenazine* - *mono* - N - *oxide* (**14a**). General procedure B was used on 50 mg, 0.14 mmole, of 2,3 - diphenyl - mono N - oxide. The product, **13a**, 40 mg, 51% was identical with authentic **13a**.

Reduction of **13a** *and* **14a**. Methanolic solns of di - N - oxide **13a** or mono - N - oxide **14a** were treated separately with aq $Na_2S_2O_4$. The solns were heated briefly and water was added to induce crystallization. Both reactions yielded 2,3-diphenylphenazine, **15**, as a yellow solid, 50%, m.p. 170–172°. IR ν_{max} 3050, 1500, 1460, 1435, 1360, 1190, 1120, 890, 855, 780, 750, 700 cm^{-1}. (Found: C, 86.66; H, 4.84; N, 8.38. Calc. for $C_{24}H_{16}N_2$: C, 86.72; H, 4.85; N, 8.43%).

2 - *Styrylquinoxaline* - 1,4 - *dioxide* (**18**). Procedure C was followed. 2 - Methylquinoxaline - 1,4 - dioxide (1.76 g, 10 mmole), benzaldehyde (3 g, 28 mmole) in MeOH (40 ml). 12 hr, 18, 1.7 g, 65%, m.p. 228–230° ($CHCl_3$–MeOH). IR ν_{max} 3020, 1625, 1530, 1500, 1375, 1240, 1220, 1090, 970, 770, 760, 745, 690 cm^{-1}. (Found: C, 73.08; H, 4.55; N, 10.70. Calc. for $C_{16}H_{12}O_2N_2$: C, 72.71; H, 4.58; N, 10.60%).

REFERENCES

[1] M. J. Abu El-Haj, B. W. Dominy, J. D. Johnston, M. J. Haddadin and C. H. Issidorides, *J. Org. Chem.* **37**, 589 (1972).

[2a] I. Yosioka and S. Uehara, *J. Chem. Soc.* Japan **78**, 351 (1958); [b] M. Weigle and L. Leimgruber, *Tetrahedron Letters* 715 (1967); [c] A. R. Katritzky and J. M. Lagowski, *Chemistry of Heterocyclic N-Oxides*, p. 19. Academic Press, London (1971).

[3] C. H. Issidorides and M. J. Haddadin, *J. Org. Chem.* **31**, 4067 (1966).

[4] R. H. Riley, J. F. Morley and N. A. Friend, *J. Chem. Soc.* 1875 (1932).

[5] J. Hamer and A. Macaluso, *Chem. Rev.* **64**, 474 (1964).

[6] J. C. E. Simpson, *The Chemistry of Heterocyclic Compounds: Cinnolines, Phthalazines and Quinoxalines*, p. 232 Interscience, New York (1953).

[7] F. B. Mallory, *Org. Synth.* Coll. Vol. IV, 74 (1963).

[8] G. R. Clemo and H. McIlwain, *J. Chem. Soc.* 479 (1938).

[9] G. A. Swan and D. G. E. Felton, *The Chemistry of Heterocyclic Compounds: Phenazines*, p. 83. Interscience, New York (1957).