

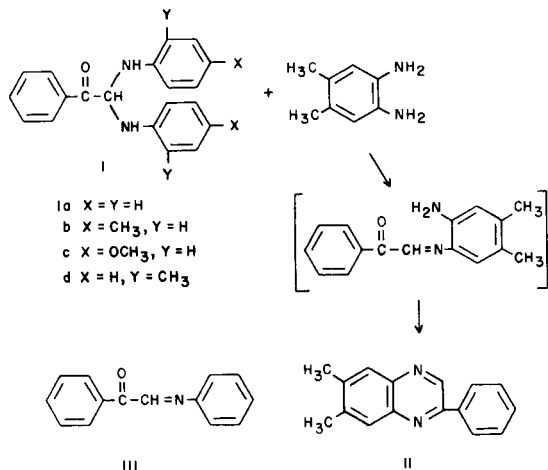
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Amination of α,α -diaminoketones I by 4,5-dimethyl-*o*-phenylenediamine gave 6,7-dimethyl-2-phenylquinoxaline (II) in a high yield. The reaction may occur through formation of α -ketoazomethine III. The α,α -diaminoketones were obtained by condensation of phenylglyoxal and substituted anilines.

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The classical synthesis of quinoxalines involves the condensation of *o*-phenylenediamine with glyoxal or α -dicarbonyls [1]. 2-Phenylquinoxalines were prepared from *o*-phenylenediamines and phenacyl chloride or different β -ketosulfoxides which behave as 1,2-diketones upon treatment with 1,2-diamino compounds in 35-65% yield [2-6]. In this paper a route to 2-phenylquinoxaline, in high yield, involves the amination of a series of α,α -diaminoketones I in a one step reaction has been described. Condensation of anilines with phenylglyoxal in ethanol gave I in 92% yield. The direct fusion, for five minutes, of Ia-d with 4,5-dimethyl-*o*-phenylenediamine gave 6,7-dimethyl-2-phenylquinoxaline (II) in about 88% yield and the corresponding amine from which the α,α -diaminoketone is derived. The reaction is basically akin to the preparation of hydroxypyrazines from α -aminoketones and bromoacetyl bromide, followed by amination and oxidation [7,8]. The product II, from every case, was compared with that derived directly from the condensation of 4,5-dimethyl-*o*-phenylenediamine and phenylglyoxal in ethanol by melting point, microanalysis, ir and uv spectrophotometry, and it has been found that they have the same structure. The reaction of I with dimethyl-*o*-phenylenediamine may occur through formation of α -ketoazomethine III intermediate. In a separate experiment, the reaction of Ia with aniline yielded compound III.



EXPERIMENTAL

Measurements of the elemental analyses, infrared and ultraviolet spectra were discussed elsewhere [9].

 α,α -Diaminoketones I.

These compounds were obtained in a yield of 92% by boiling, for five minutes, of one mole of phenyl glyoxal and two moles of the corresponding amine in ethanol. On cooling, a yellow crystalline product in every case separated and was collected and recrystallized from cyclohexane.

Compounds Ia-d have the following ir spectral data, ir (nujol mull): ν 3500-3260 cm^{-1} (N-H), 1690-1670 cm^{-1} (C=O).

2,2-Dianilino-1-phenylethanone (Ia).

Compound Ia was produced from the reaction of phenylglyoxal and aniline, mp 98°; uv (cyclohexane): λ nm (log ϵ), 280 sh (3.04), 240 (3.42).
Anal. Calcd. for C₂₀H₁₈N₂O: C, 79.47; H, 5.96; N, 9.27. *Found:* C, 79.42; H, 6.06; N, 9.25.

2,2-Di-(4-methylanilino)-1-phenylethanone (Ib).

Compound Ib was formed in the reaction of phenylglyoxal and 4-methylaniline, mp 118°; uv (cyclohexane): λ nm (log ϵ), 290 (2.63), 245 (3.37).
Anal. Calcd. for C₂₂H₂₂N₂O: C, 80.00; H, 6.67; N, 8.49. *Found:* C, 80.03; H, 6.71; N, 8.41.

2,2-Di-(4-methoxyanilino)-1-phenylethanone (Ic).

This compound was formed in the reaction of phenylglyoxal and 4-methoxyaniline, mp 122°; uv (cyclohexane): λ nm (log ϵ) 336 sh (2.48), 300 (2.75), 244 (3.31).

Anal. Calcd. for C₂₂H₂₂N₂O₃: C, 72.93; H, 6.08; N, 7.74. *Found:* C, 72.85; H, 6.07; N, 7.69.

2,2-Di-(2-methylanilino)-1-phenylethanone (Id).

Compound Id was formed in the reaction of phenylglyoxal, mp 73°; uv (cyclohexane): λ nm (log ϵ), 283 sh (2.76), 243 (3.35).

Anal. Calcd. for C₂₂H₂₂N₂O: C, 80.00; H, 6.67; N, 8.49. *Found:* C, 79.94; H, 6.71; N, 8.39.

6,7-Dimethyl-2-phenylquinoxaline (II).

Method A.

This compound was prepared by boiling equimolar quantities of phenylglyoxal and 4,5-dimethyl-*o*-phenylenediamine in ethanol for five minutes. On cooling, a yellowish-brown crystalline product separated and was collected. The product was recrystallized from cyclohexane, mp 133°.

Anal. Calcd. for C₁₆H₁₄N₂: C, 82.10; H, 5.98; N, 11.97. *Found:* C, 82.10; H, 5.98; N, 11.94.

Method B.

Compound II was prepared by direct fusion of equimolar quantities of I and 4,5-dimethyl-*o*-phenylenediamine. On cooling, in every case a solid

mass separated. The solid was filtered and recrystallized from cyclohexane, yellowish-brown needles, mp 133°; uv (cyclohexane): λ nm (log ϵ), 359 sh (2.99), 342 (3.14), 269 sh (3.54), 264 (3.55), 288 sh (3.29), 216 sh (3.49), 210 (3.53); ir (nujol mull): ν 1530 cm^{-1} (C \equiv N).

Anal. Calcd. for C₁₆H₁₄N₂: C, 82.05; H, 5.98; N, 11.97. Found: C, 82.03; H, 5.98; N, 11.94.

Phenylglyoxylideneaniline (III).

This compound was prepared by refluxing, for 70 minutes, equimolar quantities of aniline and Ia. The oily mass that formed was crystallized from cyclohexane forming a yellowish-brown crystalline product. The product was recrystallized from cyclohexane, mp 156-158°.

Anal. Calcd. for C₁₄H₁₁NO: C, 80.38; H, 5.26; N, 6.70. Found: C, 80.26; H, 5.22; N, 6.79.

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