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# BISAMINOPHENYLQUINOXALINES

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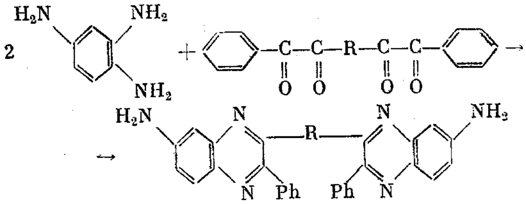
Aromatic diamines are widely used as the starting compounds in polycondensation reactions and, in particular, in the synthesis of high-molecular-weight polyamides [1] and polyimides [2].

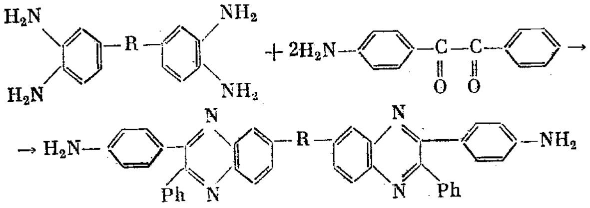
The present paper is devoted to developing methods for the preparation of some new aromatic diamines, and specifically the bisaminophenylquinoxalines, which are used in the synthesis of heat-resistant polyimidophenylquinoxalines [3].

The synthesis of the type A bisaminophenylquinoxalines was based on the reaction of 1,2,4-triaminobenzene hydrochloride with bis(α-diketones) in either dioxane — water or DMF — water mixture [4].



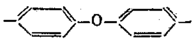
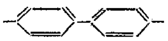
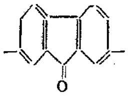
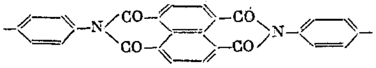
(A)

The type B bisaminophenylquinoxalines were obtained by the reaction of aromatic tetraamines with 4-aminobenzil in refluxing ethanol [5]



(B)

TABLE 1. Type A Bisaminophenylquinoxalines

| Compound | R | Yield, % | mp., °C | $\frac{\text{Found}}{\text{Calculated}}$, % C | H | N |
|---|---|---|---|---|---|---|
| (I) |  | 93 | 333–335 | $\frac{78,11}{79,05}$ | $\frac{4,50}{4,68}$ | $\frac{16,03}{16,27}$ |
| (II) |  | 95 | 205–207 | $\frac{78,07}{78,02}$ | $\frac{4,79}{4,64}$ | $\frac{13,32}{13,81}$ |
| (III) |  | 94 | 256–258 | $\frac{80,13}{81,06}$ | $\frac{4,49}{4,76}$ | $\frac{13,67}{14,18}$ |
| (IV) |  | 90 | 308–310 | $\frac{78,81}{79,59}$ | $\frac{4,12}{4,24}$ | $\frac{13,00}{13,58}$ |
| (V) |  | 87 | 460 | $\frac{74,92}{75,69}$ | $\frac{3,94}{3,75}$ | $\frac{12,92}{13,08}$ |

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Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 458-460, February, 1978. Original article submitted April 27, 1977.

0568-5230/78/2702-0396$07.50

TABLE 2. Type B Bisaminophenylquinoxalines

| Compound | R | Yield, % | mp., °C | Found / Calculated, % |  |  |
|---|---|---|---|---|---|---|
|  |  |  |  | C | H | N |
| (I) | O | 93 | 246–248 | 78,64 / 78,92 | 4,83 / 4,64 | 13,49 / 13,81 |
| (II) | – | 94 | 373–375 | 80,49 / 81,06 | 4,98 / 4,76 | 14,03 / 14,18 |
| (III) | $SO_2$ | 86 | 288–290 | 72,63 / 73,15 | 4,88 / 4,30 | 12,95 / 12,80 |

The type A and B bisaminophenylquinoxalines are characterized in Tables 1 and 2. The bisaminophenylquinoxalines are powders that range in color from yellow to dark brown; their structure was confirmed by the elemental analysis data and the IR spectra, in which the absorption bands at 1680 $cm^{-1}$, which characterize the stretching vibrations of the C=O groups in the starting bis(α-diketones), are absent, and absorption bands in the 3200-3400 $cm^{-1}$ region, which characterize the stretching vibrations of the $NH_2$ groups, are present [6].

## EXPERIMENTAL

*Type A Bisaminophenylquinoxalines.* A stirred mixture of 0.01 mole of the bis(α-diketone), 0.022 mole of 1,2,4-triaminobenzene hydrochloride, and 80 ml of a 1 : 1 dioxane — water mixture was refluxed for 7 h in an argon stream. When 2,7-bis(phenylglyoxalyl)fluorenone (tetraketone (IV), see Table 1) was used the reaction was run for 12 h in a 3 : 2 DMF — water mixture. After cooling, the mixture was poured into excess conc. aqueous ammonia solution, and after 30 min the precipitate was filtered, washed with water until neutral, then with ethanol, and dried. Compounds (I)-(IV) were purified by recrystallization from a dioxane — water mixture, while a m-cresol — methanol mixture was used in the case of (V).

*Type B Bisaminophenylquinoxalines.* Obtained by refluxing a stirred mixture of 0.004 mole of 4-aminobenzil, 0.002 mole of the tetramine, and 20 ml of ethanol in an argon stream for 15 h. After cooling the mixture the precipitate was filtered, washed with ethanol, and dried; it was purified by recrystallization from either a benzene — hexane or DMF — water mixture.

## CONCLUSIONS

Some new bisaminophenylquinoxalines were obtained, in which the $NH_2$ group is either attached directly to the phenylquinoxaline ring or through a p-phenylene nucleus.

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