SYNTHESIS OF ESTERS OF o-DICARBOXYLIC ACIDS OF THE QUINOXALINE SERIES

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Esters of substituted quinoxaline-2,3-dicarboxylic acids (Table 1), which are intermediates in the synthesis of heterocyclic analogs of phthalocyanin [2,3], were synthesized by the condensation of aromatic o-diamines with esters of diketosuccinic acid [1]. A similar condensation is described only in the case of a heterocyclic o-diamine – 2,3-diaminoquinoxaline [4]. 2,3-Dihydroxyquinoxaline was isolated instead of the expected ester of quinoxalinedicarboxylic acid in [5] by the reaction of o-phenylenediamine with diethyl diketosuccinate; however, we were able to obtain the normal condensation products by using pure starting ester.

EXPERIMENTAL

General Method of the Condensation. A mixture of 1 mmole of o-diamine and 1.25 mmole of diester of diketosuccinic acid in 5 ml of ethanol (or methanol) was refluxed for 3-4 h with stirring and cooled to

TABLE 1. Esters of Substituted Quinoxaline-2,3-dicarboxylic Acids*

Compound	mp	Empirical formula	λ_{max}, nm (lg ε)	Yield, %
Diethyl quinoxaline-2,3-dicarboxylate	82-83 [6]			40
Diethyl 5,6,7,8-Tetrachloroquinoxaline-2,3-dicarboxylate	143-144	$C_{14}H_{10}Cl_4N_2O_4$	296 (4.71), 340 (3.78)	47
Diethyl 6-Nitroquinoxaline-2,3-dicarboxylate	81-82	$C_{14}H_{13}N_3O_6$	260 (4.42)	59
Dimethyl Benzo[g]quinoxaline-2,3-dicarboxylate	174-175	$C_{16}H_{12}N_2O_4$	284 (4.89), 360 (3.63), 380 (3.67)	53
Diethyl 5,6-Phthaloylquinoxaline-2,3-dicarboxylate	167-169	$C_{22}H_{16}N_2O_6$	255 (4.62), 350 3.83	60
Diethyl 6,7-phthaloylquinoxaline-2,3-dicarboxylate	182-183	$C_{22}H_{16}N_2O_6$	292 (4.67)	60
Diethyl Naphtho[2,3-f]quinoxaline-2,3-dicarboxylate	144-145	$C_{22}H_{18}N_2O_4$	258 (4.82), 370 (3.75), 425 (3.89)	44
Diethyl Naphtho[2,3-g]quinoxaline-2,3-dicarboxylate	195-197	$C_{22}H_{18}N_2O_4$	258 (4.55), 305 (4.99), 395 (3.51), 415 (3.51), 520 (3.30)	43
Dimethyl Naphtho[2,3-g]quinoxaline-2,3-dicarboxylate	225-227	$C_{20}H_{14}N_2O_4$	258 (4.67), 307 (5.05), 397 (3.62), 417 (3.62), 520 (3.42)	57

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* Satisfactory elementary analyses were obtained for all of the compounds.

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room temperature. The crystalline precipitate was filtered, and the diester was extracted from it with alcohol. The compound was crystallized twice from alcohol with activated charcoal to obtain an analytically pure sample.

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