

Intermediates for the Preparation of Thermally Stable Polymers. IV. Symmetrical Quinoxalines and Benzoylbenzimidazoles.

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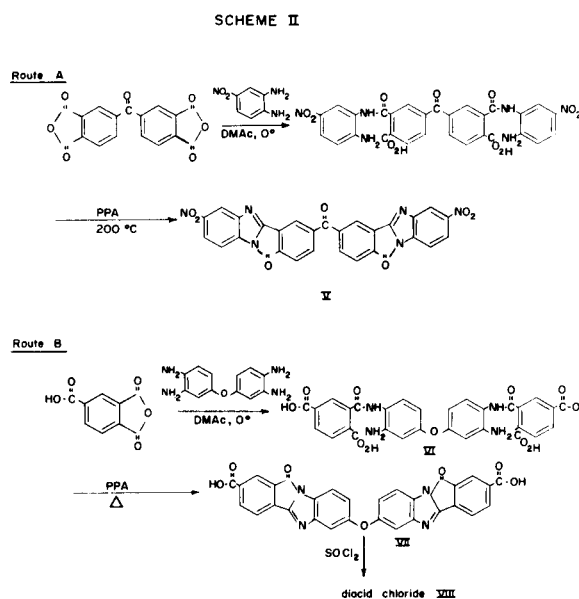
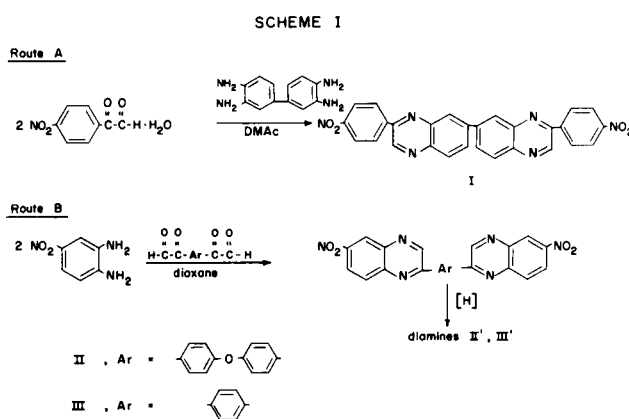
Previously we have reported symmetrical diamines and diacids containing heterocyclic rings such as oxadiazole (2), triazole (2), thiazole (2), benzimidazole (2), benzoxazole (3) and benzothiazole (3). In the present work we wish to report two additional types of intermediates – quinoxalines and benzoylbenzimidazoles – for the preparation of thermally stable ordered heterocycle copolymers (4).

The preparative route to the quinoxalines is shown in Scheme I. Although a pure benzoylbenzimidazole diamine was not prepared, it was possible to make the corresponding dinitro intermediate *via* the route shown in Scheme II (Route A); a diacid chloride containing the benzoylbenzimidazole group was prepared following the route outlined in Scheme II (Route B).

Although the syntheses reported follow along classical lines, important improvements consist of the use of dimethylacetamide (DMAc) as a superior reaction media for the synthesis of quinoxalines and the use of polyphosphoric acid to effect ring closure in the synthesis of substituted benzoylbenzimidazoles.

The quinoxalines conceivably could exist as several isomers; however, the work of Stille suggests that only one product is usually obtained (5). While the structures of our compounds were not rigorously established, the structures shown in Scheme I are in accord with those to be expected from similar compounds reported by Stille (5,6).

The experimental conditions for the synthesis of the benzoylbenzimidazole compounds were carefully controlled following the published procedures of Marvel (7) to yield compounds having the desired benzoylbenzimidazole group; the elemental analyses support the assumed presence of these groups. But the position of the nitro groups and carbonyl groups of V and VII, respectively, were not established. (Note: Although the name benzoylbenzimidazole was used above for the sake of simplicity in naming the compounds of Scheme II, rigorous application of the rules of nomenclature require that the systematic name for these compounds be that of 11H-isindolo[2-1-a]benzimidazol-11-ones as suggested to the authors by K. L. Loening, Director of Nomenclature, Chemical Abstracts Service.)



EXPERIMENTAL (8)

2,2'-bis(*p*-Nitrophenyl)-7,7'-biquinoxaline (I).

A solution of 1.00 g. (0.055 mole) of *p*-nitrophenyl glyoxal hydrate (prepared by the method of Kornblum (9) from *p*-nitrophenacyl bromide using dimethylsulfoxide as solvent and reagent) and 0.54 g. (0.0025 mole) of 3,3'-diaminobenzidine (m.p. 178-179°) in 60 ml. of dimethylacetamide was heated to reflux. After about 30 minutes, the very insoluble I precipitated. Compound I

was collected, heated with 50 ml. of dimethylacetamide to the boiling point, cooled, collected, and dried, yield, 1.2 g. The m.p. of I was 343-344°; the m.p. as determined by means of differential thermal analysis (DTA) in nitrogen was 343°.

Anal. Calcd. for $C_{28}H_{16}N_6O_4$: N, 16.86. Found: N, 16.72, 16.54.

The yield and purity of I were considerably better when carried out in DMAc rather than in dioxane (see preparations of II and II' below) or water, reaction media previously reported for synthesis of quinoxalines (5-6).

2,2'-bis(6-Nitroquinoxaline)-4,4'-diphenyl ether (II).

A solution of 8.6 g. (0.027 mole) 4,4'-oxydiphenylenediglyoxal dihydrate (5) in 100 ml. of dioxane was added dropwise over a period of two hours to a solution of 12.2 g. (0.08 mole) of 4-nitro-*o*-phenylenediamine in 100 ml. of dioxane. The solution was refluxed for 18 hours, cooled, and the product, II, collected and dried at 50° *in vacuo*; yield, 12.1 g., m.p. 276-277°.

2,2'-bis(6-Aminoquinoxaline)-4,4'-diphenyl ether (II').

Compound II, 12.0 g., in 100 ml. of dimethylacetamide was reduced catalytically using 0.5 g. of Adams catalyst. The solution was filtered to remove the catalyst, then the product was precipitated into 100 ml. of water, yield 8.8 g. of II' (m.p. 224-226°).

Anal. Calcd. for $C_{28}H_{20}N_6O$: C, 73.61; H, 4.41; N, 18.48. Found: C, 73.86, 73.83; H, 4.66, 4.10; N, 18.35, 18.35.

2,2'-*p*-Phenylene-bis(6-nitroquinoxaline) (III).

4-Nitro-*o*-phenylenediamine, 16.8 g. (0.11 mole), in 25 ml. of dioxane was reacted with 7 g. (0.031 mole) of 1,4-diglyoxalybenzene dihydrate (7) by the method described above except that the reflux time was 3.5 hours; yield of III, 6.9 g. The m.p. of III, after sublimation, was 354-355°.

2,2'-*p*-Phenylene-bis(6-aminoquinoxaline) (III').

Compound III, 6.9 g., was reduced catalytically in 100 ml. of dimethylacetamide using 0.2 g. Adams catalyst; yield of III' (m.p. 354-355°), 4.5 g.

Anal. Calcd. for $C_{22}H_{16}N_6$: C, 72.43; H, 4.42; N, 23.14. Found: C, 72.44, 72.77; H, 4.41, 7.78; N, 22.74, 22.54.

4,4'-Dicarboxy-3,3'-bis(2-amino-5-nitrobenzamido)benzophenone (IV).

To a solution of 9.2 g. (0.06 mole) of 4-nitro-*o*-phenylenediamine in 100 ml. of dimethylacetamide was added 9.7 g. (0.03 mole) of 3,3',4,4'-benzophenone tetracarboxylic dianhydride. The solution was stirred four hours, then IV was precipitated into 200 ml. of water.

Anal. Calcd. for $C_{29}H_{20}N_6O_{11}$: C, 55.38; H, 3.21; N, 13.42. Found: C, 55.25, 55.33; H, 3.67, 3.61; N, 13.39, 13.27.

2,2'-bis(8-Nitro-11 *H*-isindolo[2,1-*a*]benzimidazol-11-one)ketone (V).

Compound IV, above, was heated in 150 ml. of polyphosphoric acid at 200° for four hours; the solution of V in PPA was poured into 500 ml. of water. Compound V was washed with water and dried at 50° *in vacuo*; yield 15.2 g. of V, m.p. 345-347°.

Anal. Calcd. for $C_{29}H_{12}N_6O_7$: C, 62.55; H, 2.17; N, 15.16. Found: C, 62.69, 62.02; H, 2.50, 2.67; N, 15.07, 14.85.

Attempts to reduce V failed.

1,4-Dicarboxy-3,6-bis(2-amino-5-nitrobenzamido)benzene (V').

Pyromellitic dianhydride was substituted for 3,3',3,4'-benzophenone tetracarboxylic dianhydride in the above reaction. After sublimation of the product, a red-orange material, V' (m.p. 345-347°), was obtained.

3,3'-Diamino-4,4'-bis(2,5-dicarboxybenzamido)-diphenyl ether (VI).

To a solution of 4.6 g. (0.02 mole) of 3,3',4,4'-tetraaminodiphenyl ether (5) in 25 ml. of dimethylacetamide was added 7.7 g. (0.04 mole) trimellitic acid anhydride; the solution was stirred for two hours, then precipitated into water. The amide-acid (VI) was collected and dried; yield 12.3 g.

7,7'-bis(2-Carboxy-11 *H*-isindolo[2,1-*a*]benzimidazol-11-one) Ether (VII).

Compound VI was mixed with 50 ml. of polyphosphoric acid and the mixture heated to 140° and held at that temperature for one hour. Next, the mixture was heated at 215° for two hours. The product, VII, was precipitated in 300 ml. water, collected and dried; yield 10.5 g.

7,7'-bis(2-Chlorocarbonyl-11 *H*-isindolo[2,1-*a*]benzimidazol-11-one) Ether (VIII).

Compound VII, 10.3 g., was refluxed with 200 ml. of thionyl chloride for five hours; some unreacted diacid was filtered off and the excess thionyl chloride distilled. The residue, VIII, was recrystallized from 100 ml. of toluene to yield 3 g. of product, m.p. 259-260°.

Anal. Calcd. for $C_{30}H_{12}Cl_2N_4O_5$: N, 9.71. Found: N, 9.99.

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