Heterocyclic Intermediates for the Preparation of Thermally Stable Polymers. III. Unsymmetrical Benzoxazole, Benzothiazole and Benzimidazole Diamines

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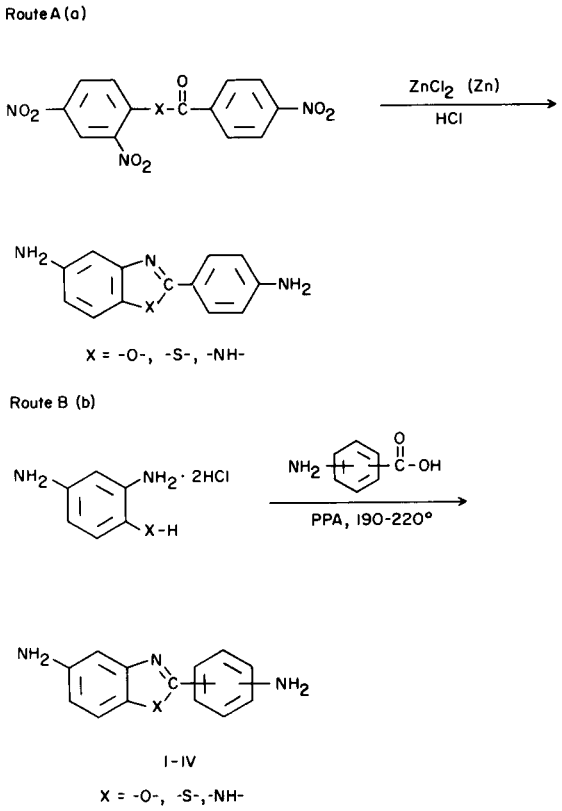
Some unsymmetrical benzoxazole, benzothiazole and benzimidazole diamines (of the types exemplified by I-IV) have been found in our laboratory and elsewhere (2) to be useful intermediates for the preparation of thermally stable polymers. However, the syntheses of such diamines (Scheme I, Route A) as reported by Kym, (3,4,5) are quite difficult to carry out and only the *para*-aminophenyl isomers were described. In his work Kym reduced trinitro esters or amides, simultaneously effecting cyclization to the heterocycle and reduction of the remaining nitro groups to amine groups.

SCHEME I



(a) Kym (3-5)

(b) Present work

In our work we have found it more convenient to prepare the diamines in a one-step synthesis which avoids reduction. The synthesis of Hein (6) employing polyphosphoric acid (PPA) as solvent and condensing agent was adopted to yield diamines according to Scheme I, Route B.

The *para* isomer of IV and another unsymmetrical heterocyclic diamine useful for the preparation of thermally stable polymers, 6-amino-2-(*p*-aminophenyl)quinoxaline (V), were prepared by reduction of their corresponding dinitro compounds. Presumably, diamines I-IV also could be prepared *via* dinitro heterocyclic intermediates; however, it was our experience that the syntheses using PPA readily gave the desired products in nearly quantitative yields and made unnecessary a separate reduction step.

EXPERIMENTAL (7)

5-Amino-2-(*p*-aminophenyl)benzoxazole (I).

A mixture of 5.9 g. (0.03 mole) of 2,4-diaminophenol dihydrochloride, 4.1 g. (0.03 mole) of *p*-aminobenzoic acid, and 50 g. of PPA was heated slowly to 110° with continuous stirring until the heavy foaming ceased, then heated to 210° and held at this temperature for 2.5 hours. (A Drierite trap was used to exclude moisture). The solution was cooled to 100° and poured into 500 ml. of water, and the precipitated product was washed with water. The crude material was soaked overnight in 250 ml. of a 10 percent aqueous sodium carbonate solution, filtered, washed with water and dried *in vacuo* at 65° yielding 5.1 g. of crude product. The pure product (see Table I) was obtained by sublimation at 135° under vacuum (0.1 mm. Hg.).

Compound II was prepared using the above procedure giving 4.9 g. of crude product. Sublimation at 250° under vacuum (0.1 mm. Hg.) afforded a pure product (Table I).

5-Amino-2-(*m*-aminophenyl)benzothiazole (III).

The 2,4-diaminothiophenol dihydrochloride used in the synthesis of III was prepared as follows. A mixture of 13.6 g. (0.066 mole) of 1-chloro-2,4-dinitrobenzene, 8 g. of sodium sulfide, and 1 g. of sulfur, was heated under reflux with 800 ml. of ethanol for an hour after which time the color of the slurry changed from brown to bright yellow. The product of the reaction was separated

TABLE I

Unsymmetrical Heterocyclic Diamines

No.	Diamine:	Color:	M.P., °C (a)	Anal. Calcd.:	Found:
I	5-Amino-2-(*p*-aminophenyl)benzoxazole	White	236-238 (b)	C, 69.31 H, 4.92 N, 18.66	C, 69.47, 69.34 H, 5.25, 5.05 N, 18.71, 18.58
II	5-Amino-2-(*m*-aminophenyl)benzoxazole	White	257-259	C, 69.31 H, 4.92 N, 18.66	C, 68.91, 68.70 H, 5.10, 4.99 N, 18.51, 18.71
III	5-Amino-2-(*m*-aminophenyl)benzothiazole	Bright-yellow	232-324 (c)	C, 64.70 H, 4.60 N, 17.41	C, 64.95, 65.17 H, 4.98, 5.00 N, 17.11, 17.36
IV	5(6)-Amino-2-(*m*-aminophenyl)benzimidazole	Orange-yellow	258-260 (d,e)	C, 69.62 H, 5.39	C, 69.12, 69.92 H, 5.66, 5.11
V	6-Amino-2-(*p*-aminophenyl)quinoxaline	Bright-yellow	213-214 (f)	N, 23.71	N, 23.95, 23.71

(a) (7). (b) Lit. (3) m.p., 229-230° (from dilute alcohol). (c) Lit. (4) m.p. for the *para*-isomer, 237-238° (from dilute alcohol). (d) Lit. (5) m.p. for the *para*-isomer, 235-236° (from dilute alcohol); loses solvent of crystallization about 150°. (e) Melting point is obscured by decomposition in air; m.p. determined by differential thermal analysis (DTA) in nitrogen is 266°. (f) DTA (nitrogen) m.p., 212°.

by filtration while hot; the yield of *bis*-2,4-dinitrophenyl disulfide, 14.0 g.

The above disulfide was slurried with 86 ml. of ethanol and then reduced with 37.2 g. of tin using 90 ml. of concentrated hydrochloric acid at reflux. During the reaction, another 90 ml. portion of concentrated hydrochloric acid was added over a period of 70 minutes. The green solution was filtered, cooled to -68°, and stripped of hydrogen chloride and solvent *via* a freez-drying process.

The residue, including tin salts, was heated with 7.6 g. (0.055 mole) of *m*-aminobenzoic acid and 200 g. of PPA as described in the process for I, above, yielding 12.4 g. (65%) of crude product, m.p. 225-227°. The crude product was sublimed to give pure III (Table I).

5(6)-Amino-2-(*m*-aminophenyl)benzimidazole (IV).

Compound IV was prepared according to the procedure outlined above for I using *m*-aminobenzoic acid (0.3 mole) and 1,2,4-benzenetriamine dihydrochloride (0.3 mole) giving 4 g. of crude product. The m.p. of the sublimed product is shown in Table I. The corresponding *para*-isomer of IV was prepared by catalytic reduction of 5(6)-nitro-2-(*p*-nitrophenyl)benzimidazole, m.p. 362-364 (lit. (8), 358°). The color of this diamine was darker than that of IV and the melting point range was broader, probably reflecting a lower state of purity for the recrystallized product compared with a sublimed product.

6-Amino-2-(*p*-aminophenyl)quinoxaline (V).

The precursor (6-nitro-2-(*p*-nitrophenyl)quinoxaline) to V was prepared as follows. To a solution of 22.3 g. (0.11 mole) of *p*-nitrophenyl glyoxal hydrate (prepared by the method of Kornblum (9) from *p*-nitrophenacyl bromide using dimethyl sulfoxide as solvent and reagent) in 50 ml. dimethylacetamide (DMAc) was added 17 g. (0.11 mole) of 2-amino-4-nitroaniline in 150 ml. of DMAc. The mixture was heated to 130° and the heating was continued for 3.5 hours. Upon cooling, a crude product separated; the yield was 16.4 g. The m.p. of the 6-nitro-2-(*p*-nitrophenyl)quinoxaline after recrystallization from DMAc was 291-293°.

Anal. Calcd. for $C_{14}H_8N_4O_4$: C, 56.59; H, 2.72; N, 18.91. Found: C, 56.86; H, 2.83; N, 18.96.

The 6-nitro-2-(*p*-nitrophenyl)quinoxaline, 8 g., was catalytically reduced in a Parr hydrogenation apparatus at 46 psi using a palladium on charcoal catalyst. After three hours the pressure fell to 29 psi; the catalyst was filtered off and the solvent evaporated. The crude product was dissolved in 60 ml. of dilute hydrochloric acid solution and heated to 50°, cooled and made basic with 1 *N* aqueous sodium hydroxide solution. The yellow-brown precipitate had a m.p. of 206-208°, yield of crude product, 4.5 g. The properties of the sublimed product, V, are given in Table I.

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