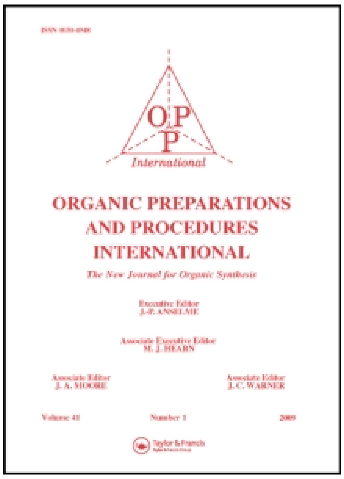

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A CONVENIENT SYNTHESIS OF 2,5-DIAMINO-1,4-BENZENEDIOL

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A CONVENIENT SYNTHESIS OF 2,5-DIAMINO-1,4-BENZENEDIOL

Submitted by (02/04/91)

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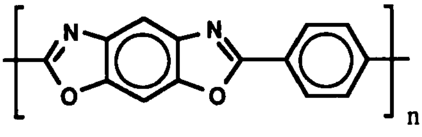
Recently, there has been considerable interest in the area of high strength liquid crystalline polymers such as poly[p-phenylenebenzobis(oxazole)] (PBO).[1] We wanted to evaluate the *trans*-isomer (**2**) for comparison and needed multi-gram quantities of 2,5-diamino-1,4-benzenediol (**5**), the precursor of **2**. The synthetic route [2,3] for compound **5** involves four steps starting from hydroquinone with a low overall yield of 18%. We report herein a novel and high-yield process for the synthesis of **5** from commercially available starting materials.



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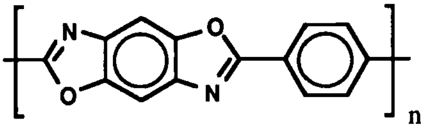
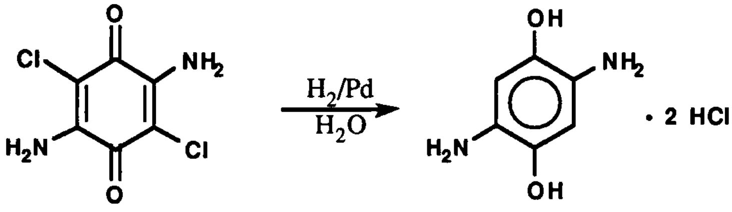


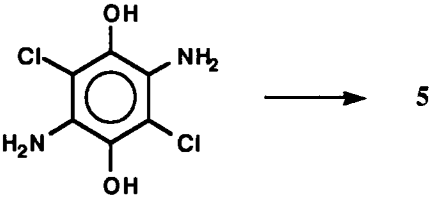
2

It is known[4,5] that *p*-chloranil, on treatment with ammonium hydroxide, undergoes selective displacement of two chlorine atoms to afford 2,5-diamino-3,6-dichlorobenzoquinone (**3**) in quantitative yield. It was reasoned that simultaneous reduction of the quinone moiety to hydroquinone as well as hydrogenolysis of the halogens in **3** should provide the desired compound **5**.



3 5

In the event, vigorous stirring of quinone 3[5] in the presence of Pd/C catalyst and hydrogen gas in a suitable solvent such as ethanol or water at ambient temperature and atmospheric pressure, provided the hydroquinone derivative 4 in quantitative yield within 4 hours. The desired dehalogenation process (conversion of 4 to 5), however, was rather slow at room temperature (2-3 days). Use of mild bases such as alkali and alkaline earth metal acetates, carbonates, and amines which are known[6] to facilitate hydrogenolysis was detrimental because of the instability of the product aminophenols under basic conditions. The reaction did not proceed at all in the presence of mineral acids presumably due to the poisoning of the catalyst by acids. It was found that direct



4

conversion of 3 to 5 (85-90% yield) could be achieved smoothly within 4 hours by maintaining a reaction temperature of 45-50° in an aqueous medium in the absence of any extraneous base. Temperatures greater than 50° lowered the yield of 5 with formation of substantial amounts of colored impurities. Although 3 is poorly soluble in water, the transformation of 3 to 4 was found to be complete within an hour at 45-50°. The water-insoluble intermediate 4 was not isolated but was allowed to react further with hydrogen under good agitation. As the dehalogenation proceeded, the product 5 was able to effectively remove the hydrogen chloride which is formed as by-product and, as the hydrochloride salt, readily went into solution thereby driving the reaction to completion. Thus, the *in situ* scavenging of HCl by 5 prevents the poisoning of the catalyst by acid and at the same time enhances the stability of the product as the hydrogen chloride salt. Small amount of stannous chloride was added to prevent the decomposition of the product during work-up and the product was isolated by filtration of the catalyst and acidification of the filtrate with conc. hydrochloric acid. Compound 5 precipitated out as the bishydrochloride salt in high purity. It is interesting to note that the reaction of 3 with hydrogen in the presence of Raney nickel as catalyst is reported to yield exclusively compound 4 in good yield.[7]

The preparation and evaluation of polymer 2 are in progress and comparison of its properties with those of polymer **1** will be published elsewhere.

EXPERIMENTAL SECTION

Melting points (uncorrected) were determined on a Thomas-Hoover capillary melting point apparatus. Proton magnetic spectrum was obtained using Varian VX300 spectrometer. Elemental analysis was carried out at the Analytical Laboratories of The Dow Chemical Company, Midland, MI.

CAUTION: ***Proper care should be exercised when handling compound 4. In general, aminophenols are toxic materials and the use of gloves, goggles, and a dust mask is recommended during the following synthesis.***

2,5-Diamino-3,6-Dichloro-1,4-Benzoquinone (**3**)[5].- A 3L 3 neck round-bottom flask fitted with a mechanical stirrer and a thermometer was charged with *p*-chloranil (231.1 g, 0.94 mol) and methoxyethyl acetate (900 mL). The well agitated slurry was heated to 60° and the heat source turned off. 27% aqueous ammonium hydroxide (360 mL) was added over 30 min with stirring. The reaction exothermed to 105° and was allowed to cool to ca. 80°. The reaction mixture was kept at 80° for 1 hr and then allowed to cool to ambient temperature. Stirring was continued overnight, the brown precipitate was filtered and washed with water (600 mL) followed by acetone (300 mL). The solid was dried in vacuum oven at 70-80° overnight to yield 188.8 g (97%) of **3** as a reddish brown solid, mp. >300°, lit.[5] no mp. given.

2,5-Diamino-1,4-benzenediol bis Hydrochloride (**5**).- A 2L round-bottom flask fitted with a mechanical stirrer, a condenser, a gas inlet tube (1cm. diameter) and a thermometer was charged with 2,5-diamino-3,6-dichloro-1,4-benzoquinone (**3**; 89 g, 0.43 mol), deionized water (700 mL), and 10% Pd/C (4 g). The heterogeneous, brown suspension was stirred vigorously (400-500 RPM) and nitrogen gas was bubbled through the mixture for 10 min. The gas inlet tube was then attached to a hydrogen cylinder and hydrogen gas was then passed through the stirred mixture. The temperature was raised to 45-50° over 1 hr and kept at that temperature for an additional 4 hrs. The suspension went into solution by this time. Bubbling of hydrogen was stopped, anhydrous stannous chloride (5 g) was added, the mixture was stirred for another 5 min, cooled to ambient temperature, filtered into 6N HCl (100 mL) and washed with water (50 mL). The pale yellow filtrate was kept under nitrogen, cooled in an ice-bath, and concd. HCl (400 mL) was added over 10 min. After 1 hr in the ice-bath, the colorless precipitate was isolated by filtration under nitrogen, washed with cold, distilled water (50 mL), cold ethanol (100 mL), and ethyl ether (400 mL). The solid was dried in vacuum oven at 70-80° (10 mm Hg) for 5 hrs to provide 79.5 g (87%) of the bishydrochloride of **5** as a colorless powder, mp. 200° (gradual darkening).

Anal. Calcd for $C_6H_{10}Cl_2N_2O_2$: C, 33.82; H, 4.73; N, 13.15
Found : C, 33.86; H, 4.83; N, 13.09

^{1}H NMR (D_2O, TMS): δ 6.96 (s, 2 H, ArH), 4.84 (br s, 8 H, 2 OH and 2 NH_3^+).

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REACTION OF 4-[bis(ALKYLTHIO)METHYLENE]-2-PHENYL-2-OXAZOLIN-5-ONES WITH AMBIDENT NUCLEOPHILES

Submitted by
(03/07/90)

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Aminolysis of 4-[bis(methylthio)methylene]-2-phenyl-2-oxazolin-5-one (**1a**) with primary amines to give N-substituted-2-benzamido-3-[bis(methylthio)]acrylamides or N,N-disubstituted benzamidomalondiamides has been reported earlier.[1] In order to exploit the bielectrophilic property of compounds of type **1**, the reaction of **1a** with several binucleophiles such as hydrazine, phenylhydrazine, *o*-phenylenediamine and *o*-aminothiophenol was investigated under both neutral and acidic conditions.

It is noteworthy that the aminolysis of **1** with binucleophiles proceeded through the cleavage of 1,5-bond[1] instead of 1,2-bond cleavage in 2-oxazolin-5-one as reported by Hanumanthu *et al.*[2] As