

SHORT  
COMMUNICATIONS

## Dechlorination of Polychloroaromatic Acids Effected by Reducing System NiCl<sub>2</sub>-2,2'-bipyridyl (or 1,10-phenanthroline)-Zn

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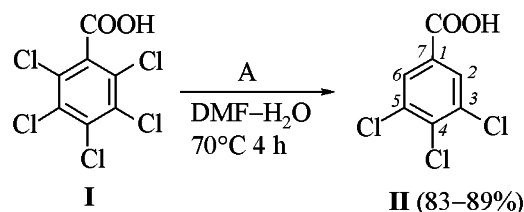
Partially chlorinated benzoic and phthalic acids, among them 3,4,5-trichlorobenzoic acid and 4,5-dichlorophthalic acid, are used in the synthesis of phthalocyanine dyes and polymers [1], of pharmaceuticals [2] etc. The synthesis of 3,4,5-trichlorobenzoic acid by oxidation of the corresponding benzophenone is described in the literature [3]. This procedure provides sufficiently high yield of the target products, affords various halobenzoic acids, but requires preliminary synthesis of initial benzophenones [3]. The 3,4,5-trichlorobenzoic acid was also obtained by hydrolysis of 3,4,5-trichlorobenzotrichloride that in its turn was prepared by trichloromethylation of 1,2,3-trichlorobenzene [4]. This procedure provides a possibility to obtain alongside the 3,4,5-trichlorobenzoic acid quite a number of various chlorobenzoic acids.; however the yields as a rule are low [4].

The published data on preparation of 4,5-dichlorophthalic acid describe the chlorination of phthalic acid catalyzed with iron chloride [5]. The arising mixture of 3- and 4-chlorophthalic acids was separated by rectification, and isomer with a chlorine in the fourth position was subjected to further chlorination to furnish a mixture of dichlorophthalic acids. Successive rectification provided the 4,5-dichlorophthalic acid in about 10% yield [5]. The disadvantages of this procedure include low yield of target products and the necessity of rectification of the products. Another described synthesis of the 4,5-dichlorophthalic acid (sodium hydrogen salt) consists in reaction between phthalic acid and chlorine in water solution of alkali at 50°C [1]. The preparative yield of the target product was 62%.

It was shown before that reaction of catalytic reducing system NiCl<sub>2</sub>-2,2'-bipyridyl (or 1,10-

phenanthroline)-Zn (system A) with polyfluorochlorobenzenes [6, 7] and with some polychloroarenes [7, 8] in aqueous dimethylformamide results in efficient dechlorination of these substrates furnishing in the former case fluorobenzenes and mixtures of partially chlorinated arenes in the latter [6-8]. At the same time we found that the catalytic system A under mild conditions and with good yield transformed the pentafluorobenzoic acid into 2,3,4,5-tetrafluoro- and 3,4,5-trifluorobenzoic acids [9]. Taking into account the above it seems feasible to study the reaction of this system with polychloroaromatic acids, such as pentachlorobenzoic and tetrachlorophthalic acid.

We showed that reaction between pentachlorobenzoic acid (I) and catalytic reducing system NiCl<sub>2</sub>-2,2'-bipyridyl (or 1,10-phenanthroline)-Zn (A) resulted in hydrogenolysis of C<sub>arom</sub>-Cl bonds in positions 2 and 6 of the benzene ring. The reaction gave rise to a mixture of 2,3,4,5-tetrachlorobenzoic and 3,4,5-trichlorobenzoic acids within 1-2 h. At prolonging the reaction to 4 h the only product was acid II in 83-89% preparative yield. The reaction was carried out at 70°C in DMF-H<sub>2</sub>O.



Dechlorination of tetrachlorophthalic acid (III) under similar conditions also resulted in replacement hydrogen for chlorine in positions neighboring to the carboxy groups and in formation of a mixture containing 3,4,5-trichlorophthalic and 4,5-dichlorophthalic

acids. Therewith in 4 h of the process the 3,4,5-trichlorophthalic acid disappeared from the reaction mixture, and acid **IV** could be isolated in preparative yield 86–90%.

The comparison of the above discussed results with the existing publications on preparation of 3,4,5-trichlorobenzoic and 4,5-dichlorophthalic acids [1, 3–5] shows the accessibility and efficiency of our preparation method for these compounds by dechlorination of pentachlorobenzoic and tetrachlorophthalic acids with the use of catalytic reducing system  $\text{NiCl}_2$ -2,2'-bipyridyl (or 1,10-phenanthroline)-Zn.

*General procedure.* From 0.065 g of nickel(II) chloride, 0.156 g of 2,2'-bipyridyl (or 0.196 g of 1,10-phenanthroline) in 10 ml of aqueous DMF (volume ratio DMF:H<sub>2</sub>O 9:1) was prepared brightly colored complex, and then 5 g of zinc powder was added thereto. After a darkly colored complex was formed to the solution was added 10 mmol of the initial acid (2.9 g of pentachlorobenzoic acid or 3 g of tetrachlorophthalic acid), and the mixture was stirred at 70°C in a flask equipped with a reflux condenser. The reaction progress was monitored by HPLC. On completion of the reaction the mixture was cooled, quenched with 50 ml of 10% solution of hydrochloric acid, and the reaction products were extracted into ether (2×25 ml). The ether was removed on a rotary evaporator. Synthesis of acid **II**: reaction time 4 h, preparative yield 83–89%. Synthesis of acid **IV**: reaction time 4 h, preparative yield 86–90%.

**3,4,5-Trichlorobenzoic acid (II).** mp 164–165°C (publ. 164°C [4]). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 8.01 (2H). <sup>13</sup>C NMR spectrum,  $\delta$ , ppm: 130.39 (C<sup>2</sup>, C<sup>6</sup>),

131.94 (C<sup>1</sup>), 134.86 (C<sup>3</sup>, C<sup>5</sup>), 136.02 (C<sup>4</sup>), 164.69 (C<sup>7</sup>).

<sup>1</sup>H and <sup>13</sup>C NMR spectra of reaction products were registered on spectrometers Bruker WP200SY and Bruker DRX500 respectively, internal reference HMDS ( $\delta$  0.04 ppm), solvent acetone-*d*<sub>6</sub>. Elemental composition was determined on Finnigan MAT 8200 instrument. Chromatographic analysis was carried out on liquid chromatograph Milichrom-4-equipped with a column 62×2 mm packed with a sorbent Separon S-18, 5 $\mu$ . As detector served UV spectrophotometer on wavelengths 230 and 254 nm. Eluent aqueous acetonitrile, 60 and 70%.

The melting point, <sup>1</sup>H and <sup>13</sup>C NMR spectra of compound **IV** were consistent with the published data [5].

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