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LETTERS TO THE EDITOR

Diphosphono- and Chlorophosphonobenzene-1,2-dicarboxylic Acids

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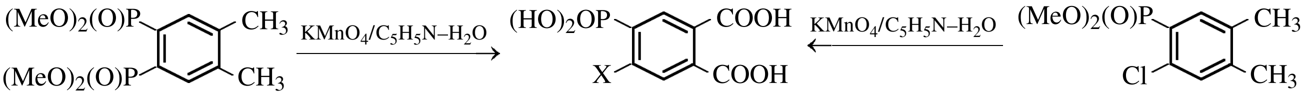
o-Phenylenebis(phosphonates) and *o*-chlorophenylphosphonates are interesting synthons for polydentate ligands [1–4]. Earlier we proposed a general synthetic strategy for alkyl-substituted *o*-ophenylenebis(phosphonates) and *o*-chlorophenylphosphonates, where the *ortho* arrangement of substituents was provided by forming a six-membered ring by the Diels–Alder reaction of donor 1,3-alkadienes and (ethyne-1,2-diyl)bis(phosphonic acid) or chloroethynephosphonic acid as dienophiles. Ring aromatization was achieved by the action of the $KMnO_4/Al_2O_3$ system [5].

Aimed at creating new effective complex-forming agents, we turned to searching for ways to further functionalization of *o*-phenylenebisphosphonates and *o*-chlorophenylphosphonates. In the present work we studied oxidation by $KMnO_4$ of the 4- and 5-Me groups in such derivatives, that appear when the Diels–Alder condensation is performed with 2,3-dimethylbutadiene. The oxidation was accompanied by hydrolysis of the phosphonates and resulted in formation of earlier unknown phosphorus-containing derivatives of phthalic acid, viz. 4,5-diphosphonobenzene-1,2-dicarboxylic acid (**IIa**) and 4-chloro-5-phosphono-1,2-dicarboxylic acid (**IIb**).



Ia **IIa, IIb** **Ib**

X = $P(O)(OH)_2$ (**a**), Cl (**b**).

Compounds **Ia** and **Ib** are easily oxidized by $KMnO_4$ in boiling aqueous pyridine with high yield of the target products. A significant excess of $KMnO_4$ is required, because it is consumed for oxidation of the methanol formed by hydrolysis. Acids **IIa** and **IIb** can also be prepared in the aqueous medium but in a considerably lower yield. The products are high-melting crystalline substances readily soluble in water and methanol.

4,5-Diphosphonobenzene-1,2-dicarboxylic acid (IIa). To a boiling and stirred solution of 9.7 g of 4,5-dimethyl-*o*-phenylenebis(dimethyl phosphonate) (**Ia**) in 50 ml of 50% aqueous pyridine, $KMnO_4$ was slowly added until the violet color no longer disappeared (a total of ~57 g). The reaction mixture was refluxed for 2 h, and then cooled and filtered. The MnO_2 precipitate was washed with 50 ml of hot water. The filtrate was acidified with conc. HCl (test by universal indicator), evaporated to dryness at reduced pressure, and the residue was dried. The dry material was treated with hot dioxane (3 × 30 ml), the dioxane was distilled off, and the residue was dried for 8 h at 120–130°C and recrystallized from 1,4-dioxane–MeOH (3 : 1). Yield 60%, mp 332–335°C (decomp.). ^{1}H NMR spectrum, δ, ppm: 8.64 m (2H, $^3J_{HP}$ 15.2 Hz), 4.60 s (6OH, H_2O). ^{13}C NMR spectrum, δ_C, ppm: 173.92 s ($C^{7,8}$), 140.60 d.d ($C^{1,2}$, $^1J_{CP}$ 172.34, $^2J_{CP}$ 10.4 Hz), 141.47 d (C4,5, $^3J_{CP}$ 11.3 Hz), 135.04

d.d ($C^{3,6}$, $^2J_{CP} = {}^3J_{CP}$ 9.3 Hz). ^{31}P NMR spectrum (D_2O), δ_P, ppm: 6.22 s.

4-Chloro-5-phosphonobenzene-1,2-dicarboxylic acid (IIb) was prepared by the same procedure from 7.4 g of dimethyl (2-chloro-4,5-dimethylphenyl)phosphonate (**Ib**) under the action of 47.4 g of $KMnO_4$. Yield 75%, mp 310–314°C (decomp.; from dioxane–MeOH, 3 : 1). ^{1}H NMR spectrum, δ, ppm: 8.33 d (1H, $^3J_{HP}$ 14.04 Hz), 7.71 d (1H, $^4J_{HP}$ 4.9 Hz), 4.80 s (4OH, H_2O). ^{13}C NMR spectrum, δ_C, ppm: 171.92 s (C^8), 171.44 s (C^7), 140.77 d (C^5, $^3J_{CP}$ 4.9 Hz), 137.40 d (C^1, $^1J_{CP}$ 178.1 Hz), 137.08 s (C^4), 135.39 d (C^6, $^2J_{CP}$ 8.8 Hz), 131.66 d (C^3, $^3J_{CP}$ 8.7 Hz), 129.93 d (C^2, $^2J_{CP}$ 11.8 Hz). ^{31}P NMR spectrum (D_2O), δ_P, ppm: 5.97 s.

The ^{1}H, ^{13}C and ^{31}P NMR spectra were registered on a Bruker AC-200 instrument at 200.05 (^{1}H), 50.328 (^{13}C) and 81 (^{31}P) MHz, solvent D_2O. The chemical shifts were measured against internal $CDCl_3$ (^{13}C, ^{1}H) and external 85% H_3PO_4 (^{31}P). All reagents were of chemical grade.

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