[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DE PAUL UNIVERSITY]

Preparation of Some *o*-Substituted Cyclohexylbenzenes

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Few *o*-substituted derivatives of cyclohexylbenzene have been prepared, owing largely to steric interference with *o*-substitution by the cyclohexyl group. Mayes and Turner[3] separated *o*-nitrocyclohexylbenzene from a mixture containing 38% *o*- and 62% *p*-isomer obtained by nitration with fuming nitric acid in glacial acetic acid solution. Neunhoffer[4] obtained a small quantity of the *o*-amino derivative by electrolytic reduction of the *o*-nitro compound, while Boudroux and Thomassin[5] have prepared *o*-cyclohexylphenol.

The present investigation was undertaken for the purpose of increasing the availability of these and other *o*-substituted cyclohexylbenzenes through electrolytic reduction of *o*-nitrocyclohexylbenzene to the amine. Neunhoffer[4] carried out such a reduction in an apparatus described by Müller.[6] Inasmuch as reduction of the *o*-nitro compound with tin or iron and hydrochloric acid proved unsatisfactory, electrolytic reduction, giving 85% yields of the corresponding amine, was employed in this work. Through diazotization of the amine, the corresponding *o*-chloro, bromo, and iodocyclohexylbenzenes and *o*-cyclohexylbenzonitrile were readily prepared.

Experimental

The *o*-nitrocyclohexylbenzene used in this work was prepared by the method of Mayes and Turner.[3]

***o*-Aminocyclohexylbenzene.**—Reduction of *o*-nitrocyclohexylbenzene was carried out electrolytically in an apparatus similar to that described by Müller[6] and also by Elbs,[7] modified for use on a large scale. This included a porous cup 3 inches in diameter placed in a 4-liter beaker, a sheet lead anode, a mercury cathode and a mechanical stirrer.

In a typical run the catholyte, consisting of a mixture of 137 g. of *o*-nitrocyclohexylbenzene, 167 ml. of concentrated hydrochloric acid, 700 ml. of distilled water, 122 ml. of 96%, and 6.6 g. of stannous chloride dihydrate, was heated almost to its boiling point and placed in the cell and reduced just below the boiling point with a 10-ampere current for thirteen hours. Completion of the reduction was indicated by a rapid evolution of hydrogen. Evaporation of the solution on a steam-bath until most of the alcohol was expelled caused the amine hydrochloride, which is relatively insoluble in water, to separate as a violet colored oil on cooling. This was washed with water and converted to the free amine by stirring with 250 ml. of 20% sodium hydroxide at 80°. The amine was extracted with ether, the extract dried over solid sodium hydroxide, the ether evaporated and the product distilled, giving 98.2 g. of amine (84.9%), b. p. 132–134° (3 mm.). Neunhoffer[4] reported a boiling point of 106° (0.5 mm.).

***o*-Aminocyclohexylbenzene Hydrochloride.**—The amine hydrochloride prepared with aqueous hydrogen chloride is difficult to purify. It was therefore prepared by precipitation from ether solution, with stirring, by anhydrous hydrogen chloride. On recrystallization from warm ether it was obtained in sheaf-like clusters of needles, m. p. 107.8° (cor.).

***o*-Chlorocyclohexylbenzene.**—Sixteen grams of *o*-aminocyclohexylbenzene hydrochloride was diazotized in the usual manner and converted into *o*-chlorocyclohexylbenzene by the action of hydrochloric acid and cuprous chloride. Extraction with ether, washing and drying, gave 10.1 g. of impure product. Distillation gave 4.2 g. (30.4%) of pure *o*-chlorocyclohexylbenzene, b. p. 118–120° (3 mm.), $n^{24}\mathrm{D}$ 1.5429, d^{24}_{24} 1.0706, $Z^{24}\mathrm{D}$ 4.16, $M\mathrm{D}$ 57.24. Oxidation by alkaline permanganate produced *o*-chlorobenzoic acid.

Anal. Calcd. for $C_{12}H_{15}Cl$: Cl, 18.23. Found: Cl, 18.19.

***o*-Bromocyclohexylbenzene.**—Fifteen grams of *o*-aminocyclohexylbenzene hydrochloride was diazotized and converted into the corresponding *o*-bromo derivative with hydrobromic acid and cuprous bromide. There was obtained 11.4 g. of impure, and 4.6 (27.3%) of pure product, b. p. 128–130° (5 mm.), $n^{24}\mathrm{D}$ 1.5616, d^{24}_{24} 1.2953, $Z^{24}\mathrm{D}$ 4.08, $M\mathrm{D}$ 59.78. Oxidation gave *o*-bromobenzoic acid.

Anal. Calcd. for $C_{12}H_{15}Br$: Br, 33.43. Found: Br, 33.44.

***o*-Iodocyclohexylbenzene.**—Thirteen grams of *o*-aminocyclohexylbenzene hydrochloride was diazotized and converted to the *o*-iodo compound by means of potassium iodide solution. Separation and distillation gave 5.8 g. (32.3%) of pure *o*-iodocyclohexylbenzene, b. p. 159–160° (5 mm.), $n^{24}\mathrm{D}$ 1.5920, d^{24}_{24} 1.4670, $Z^{24}\mathrm{D}$ 3.78, $M\mathrm{D}$ 65.51. Oxidation converted it into *o*-iodobenzoic acid.

Anal. Calcd. for $C_{12}H_{15}I$: I, 44.39. Found: I, 44.09.

***o*-Cyclohexylbenzonitrile.**—Twenty grams of amine hydrochloride was diazotized, the solution neutralized with solid sodium carbonate and run into a stirred mixture of 50 ml. of benzene with an excess of an aqueous solution of cuprous cyanide. Separation and distillation of the benzene gave 3.4 g. (19.4%) of pure *o*-cyclohexylbenzonitrile, b. p. 149–151° (5 mm.), $n^{24}\mathrm{D}$ 1.5171, d^{24}_{24} 1.0016, $Z^{24}\mathrm{D}$ 4.19, $M\mathrm{D}$ 55.96. Oxidation gave *o*-cyanobenzoic acid.

Anal. Calcd. for $C_{13}H_{15}N$: N, 7.57. Found: N, 7.41.

Summary

A procedure suitable for the electrolytic reduction of *o*-nitrocyclohexylbenzene in quantity is described.

The *o*-chloro, bromo and iodocyclohexylbenzenes and *o*-cyclohexylbenzonitrile have been prepared and their chief physical constants determined.

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(3) Mayes and Turner, *J. Chem. Soc.*, 500 (1929).

(4) Neunhoffer, *J. prakt. Chem.*, **133**, 95 (1932).

(5) Boudroux and Thomassin, *Compt. rend.*, **205**, 991 (1937).

(6) Müller, "Electrochemisches Praktikum," 5th ed., T. Steinkopff, Dresden, 1941, p. 212.

(7) Elbs, "Übungsbeispiele für die elektrolytische Darstellung chemischer Präparate," 2nd ed., Knapp, Halle, 1911, p. 83.