SYNTHESIS OF p-SUBSTITUTED-BENZALDEHYDE-α-d

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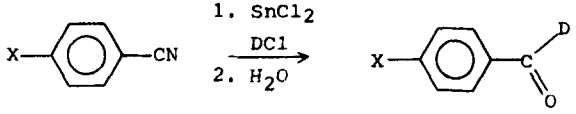
p-Substituted-benzaldehyde-α-d was prepared from p-substituted-benzonitrile in good yield. The deuterium content of each compound was calculated by pmr.

INTRODUCTION

In the reaction originated by Stephen[1] for the conversion of a nitrile to an aldehyde, an ether solution of the nitrile is added to a stannous chloride solution saturated with hydrogen chloride. The best results are obtained in the aromatic series.

In our study, hydrogen chloride was replaced with deuterium chloride and p-substituted-benzaldehyde-α-d was prepared accordingly.



X = H, CH_3, Cl

Wiberg[2] prepared benzaldehyde-α-d by reduction of benzoin with $LiAlD_4$ followed by treatment of the resulting dihydrobenzoin-d_2 with lead tetraacetate. Our method provides an alternative with a simple one-step reaction.

The deuterated products were obtained in high yield (72 - 82%) with more than 90% deuteration. Benzaldehyde-α-d was identified by ir with two aldehyde C-D stretching bands at 2100 and 2045 cm^{-1},[2] and by pmr. The deuterium contents of benzaldehyde-α-d and p-chlorobenzaldehyde-α-d were calculated from the numbers of

aldehyde proton using phenyl protons as reference, whereas that of p-tolualdehyde-α-d was calculated using phenyl protons and methyl protons as references.

EXPERIMENTAL

Benzaldehyde-α-d. In a 2 l., 3-necked round-bottomed flask, provided with a mechnical stirrer, a dry ice-acetone reflux condenser carrying a $CaCl_2$ drying tube, and a gas inlet tube reaching to the bottom of the flask, were placed 190 g (1 mol) of anhydrous $SnCl_2$ prepared by dehydrating $SnCl_2$ dihydrate with acetic anhydride, and 1 l. of anhydrous ether. While the mixture was vigorously stirred, dry deuterium chloride generated by heating a mixture of 1 l. benzoyl chloride and 50 ml of 99.8% D_2O at ca. 100°[3] was introduced through the inlet tube. The saturation of the $SnCl_2$ with DCl required 4-5 hours. At the end of this period, the $SnCl_2$ formed a viscous lower layer. The inlet tube was replaced by a dropping funnel, and a solution of 51.5 g (0.5 mol) benzonitrile in 100 ml anhydrous ether was added rapidly. The solution was then stirred vigorously for 1 hr and allowed to stand for 12 hr. The ethereal solution was decanted from the white crystalline product, which was then rinsed with two 200 ml portions of ether. About 300 ml of water was added to the solid, and steam distillation was carried out by immersing the flask in an oil bath at 110°-120° and passing steam through the solution. The distillation was stopped after about 1.5 l. of distillate was collected. The distillate was extracted with ether, and the ether extract was dried overnight over anhydrous sodium sulfate. Distillation gave 39 g of product (72%), bp 76°/20 mm, ir, two aldehyde C-D stretching bands at 2100 and 2045 cm^{-1}, identical with those reported by Wiberg, using a different preparative method, pmr, δ 9.90 (s, 0.101 H, aldehyde proton), 7.75 (d, 2 H, o-phenyl protons), 7.42 (m, 3 H, m- and p-phenyl protons), indicating 0.899 atom D per molecule.

p-Tolualdehyde-α-d. The deuterated aldehyde was prepared from p-tolunitrile(Aldrich) in the same way as the unsubstituted analog, yield 78%, bp 73°/10 mm (lit[4] bp for undeuterated compound, 204-5°, ir, 1705 cm^{-1} (C=O stretching), pmr, δ 9.80 (s, 0.041 H, aldehyde proton), 7.63 (d, 2 H, o-phenyl protons), 7.18 (d, 2 H, m-phenyl protons), 2.34 (s, 3 H, methyl protons), indicating 0.959 atom D per molecule.

p-Chlorobenzaldehyde-α-d. The deuterated aldehyde was prepared from p-chlorobenzonitrile(Aldrich) in the same way as the unsubstituted analog, yield 82%, bp 58°/2 mm, mp 46° (lit[5] bp and mp for undeuterated compound, 108-11°/25 mm and 47°), pmr, δ 9.95 (s, 0.095 H, aldehyde proton), 7.68 (d, 2 H, o-phenyl protons), 7.21 (d, 2 H, m-phenyl protons), indicating 0.905 atom D per molecule.

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