SYNTHESIS OF 1,2-BENZENEDICARBOXALDEHYDE-D_6 THROUGH THE OZONIZATION OF NAPHTHALENE-D_8

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SUMMARY

Naphthalene-d_8 was ozonized and the perdeuteroozonide was directly converted to 1,2-benzenedicarboxaldehyde-d_6 by using dimethylsulfide. The perdeuteroozonide was also converted to 1,2-benzenedicarboxaldehyde-d_6 through a three step synthesis, with the following intermediates: 2-formylbenzoic acid-d_6, 2-formylbenzoic acid-d_5 methylester and 1,2-bis(hydroxymethyl-d_2) benzene-d_4. Both synthetic methods were described in detail.

Key Words: Naphthalene, Deuterium, Ozonization, Benzenedicarboxaldehyde

INTRODUCTION

There is a growing interest in perdeuterated compounds in spectroscopic research, for which now exist a variety of synthetic methods. In this article the usage of ozone is introduced in the "perdeuteration chemistry". Ozone in combination with already perdeuterated chemicals gives new possibilities in the preparation of interesting perdeuterated materials.

For the synthesis of perdeuterated pentacene 1,2-benzenedicarboxaldehyde-d_6 was needed as the starting material. One possible route was to synthesize 1,2-benzenedicarboxaldehyde-d_6 from 1,2-benzene-d_4 dicarboxamide N,N,N',N' tetramethyl by reduction with $LiAlD_4$(1). However the preparation of this starting compound, by acid-catalysed exchange of the H analog with D_2O, was not succesful. The next attampt was to synthesize the 1,2-benzene-d_4 dicarboxylic acid using the method of Buu-Hoï et al(2,3). In this case also was the resulting product not the expected acid. Attampts were then made to prepare 1,2-benzenedicarboxaldehyde-d_6 (V), following the method of Bailey et al(4). Ozonization of naphtha-

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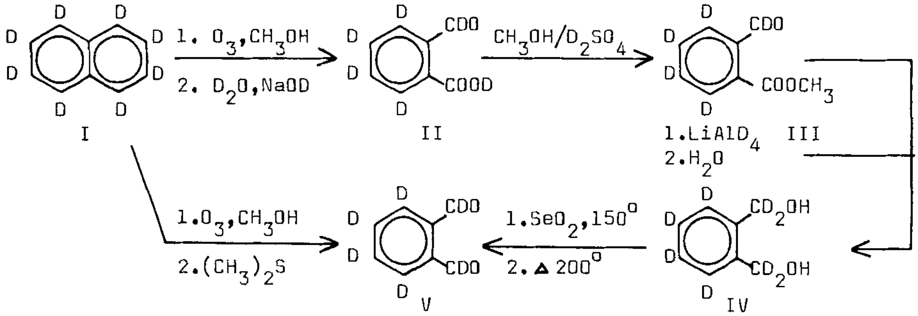
lene-d_8 (I) gave 2-formylbenzoic acid-d_6 (II) and after esterification of II with methanol 2-formylbenzoic acid-d_5 methylester (III). 1,2-Bis(hydroxymethyl-d_2) benzene-d_4 (IV) was obtained after reduction of III with $LiAlD_4$ and 1,2-benzenedicarboxaldehyde-d_6 (V) after oxidation of IV with SeO_2(5,6). The last method used was analogeous to the method of Pappas et al(7), giving 1,2-benzenedicarboxaldehyde-d_6 (V) readily from naphthalene-d_8 using ozone and dimethylsulfide.



EXPERIMENTAL

The analytical results were obtained with the following instruments: m.p., Mettler FP5/51; mass spectra, AEI-MS 9 and Micromass 12; uv, Cary 14; ir, Unicam SP 1000, measured as a liquid between KBr. Naphthalene-d_8 and $LiAlD_4$ were purchaced from E. Merck, Darmstadt, Germany.

2-Formylbenzoic acid-d_6 (II):

Naphthalene-d_8 (5 g, 37 mmol.) in dry methanol (100 ml.) was ozonized in 2½ hrs at -40 to -60°, until the solution became clear. After the solution was made free of ozone by bubbling oxygen through it, 10% NaOD in D_2O (25 ml.) was added to the solution at -40°. Overnight the mixture was allowed to come to room temperature. The solution was then refluxed for ½ hr, cooled and brought to pH 6 with DCl/D_2O, to yield 6 g oil, which was used without further purification for the next step. Ir, 2130 cm^{-1},CDO; 2580 cm^{-1},COOD.

2-Formylbenzoic acid-d_5 methylester (III):

II (6 g, 38 mmol.) was heated in a mixture of dry benzene (40 ml.), dry methanol (50 ml.) and D_2SO_4 (0.2 ml.) for 24 hrs in a Soxhlet extractor filled with 3A/4A mol. sieves. The solvent was evaporated, the resulting oil taken up in diethyl ether, washed with Na_2CO_3 solution until it was neutral, dried on Na_2SO_4 and filtered. The solvent was evaporated, the residue distilled, b.p. 180°/15 mm, yielding 3.4 g oil. Ir, 2130 cm^{-1},CDO; 2580 cm^{-1},COOD was not detectable.

1,2-Bis(hydroxymethyl-d_2) benzene-d_4 (IV):

III (3.4 g, 20 mmol.) in dry diethyl ether (100 ml.) was stirred under N_2 and $LiAlD_4$ (0.45 g, 11 mmol.) was added in 5 portions. After standing overnight the mixture was worked up, yielding 2.8 g of a white solid, m.p. 64.0°; lit. 64.2-64.8° for the H analog. Ir, in a KBr disk, 3400 cm^{-1} and 2540 cm^{-1}, broad peaks.

1,2-Benzenedicarboxaldehyde-d_6 (V):

IV (0.55 g, 3.1 mmol.) and SeO_2 (0.40 g, 3.6 mmol) were slowly heated to 150° and the water was distilled off. The dry residue was heated above 200°, the distilled product was taken up in diethyl ether, dried, the solvent removed and the residue sublimed, yielding 0.1 gr. of a white solid, m.p. 55.1°; lit. 53.2°; 56-57° for the H analog. Ir, in a KBr disk, 2120 cm^{-1},CDO; mass anal.,m/e 140, $C_8D_6O_2$; m/e 110,C_7D_5O; m/e 82,C_6D_5; m/e 54,C_4D_3.

1,2-Benzenedicarboxaldehyde-d_6 (V):

Naphthalene-d_8 (5 g, 37 mmol.) in dry methanol (100 ml.) was ozonized in 2½ hrs at -50°. The solution became clear and after it was made free of ozone, by bubbling oxygen through the solution, dimethylsulfide (10 ml.,136 mmol.) was added to the ozonide at -50°. After standing overnight the solution was worked up, yielding 1.9 g of a white solid, m.p. 54.4°. Ir, in a KBr disk, 2120 cm^{-1},CDO; mass anal., m/e 140; 110; 82; 54, the same mass spectrum as above.

Anal. calcd. C,68.55; D,8,62; found C,68.24; D,8.59 .

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