SYNTHESIS OF DEUTERATED PENTACENES

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SUMMARY

Pentacene-d_{14}, pentacene-d_{12} and pentacene-d_4 were obtained from 6,13-pentacenequinone-d_{12} and 6,13-pentacenequinone-d_4 by refluxing with aluminumcyclohexoxide-d_{33} or aluminumcyclohexoxide. The former quinones were prepared from 1,2-benzenedicarboxaldehyde-d_6 or 1,2-benzenedicarboxaldehyde-d_2 and 1,4-cyclohexanedione-d_8. The aldehydes were prepared from naphthalene-d_8 through ozonization or by reduction of 1,2-benzenedicarboxylic acid dimethylester with $LiAlD_4$. All synthetic methods were described in detail.

Key Words: Pentacene, Deuterium, Pentacenequinone, Aluminumcyclohexoxide, Benzenedicarboxaldehyde, Cyclohexanedione.

INTRODUCTION

In spectroscopic research there is a growing interest in perdeuterated compounds for which there now exist a variety of synthetic methods. This article describes the synthesis of the titled compounds from already perdeuterated chemicals.

Initialy the needed perdeuteropentacene was tried to prepare by acid-catalysed exchange of the H analog with D_2O(1) and by the use of an homogeneous catalyst and benzene-d_6(2). Both methods however were without succes. The third synthetic method followed Ried and Anthöfer(3), using 1,2-benzenedicarboxaldehyde-d_6(4) (I) and 1,4-cyclohexanedione-d_8(5)(II), to yield 6,13-pentacenequinone-d_{12} (III) 6,13-Pentacenequinone 5,7,11,14-d_4 (VII) was obtained from II and 1,2 benzenedicarboxaldehyde-d_2 (VI). The next step followed the method of Bruckner et al(6,7), by treatment of III with aluminumcyclohexoxide-d_{33} to yield the desired penta-

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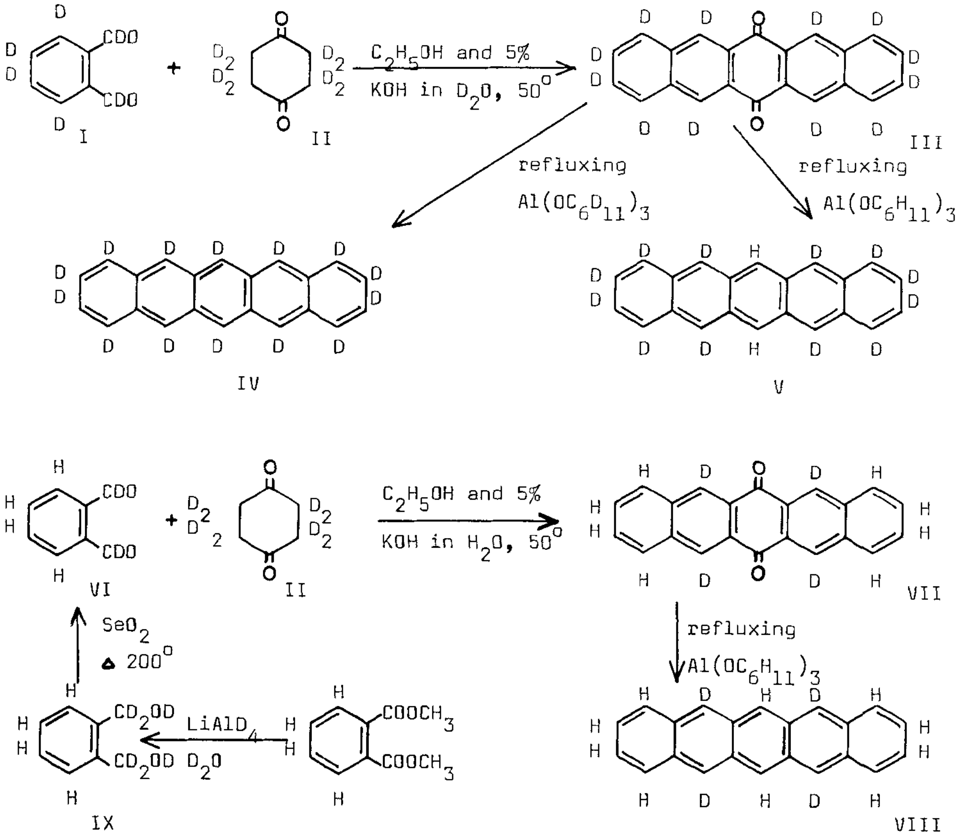
cene-d_{14} (IV). Pentacene 1,2,3,4,5,7,8,9,10,11,12,14-d_{12} (V) was obtained by treatment of III with aluminumcyclohexoxide. The final product pentacene 5,7,12,14-d_4 (VIII) was prepared from VII and aluminumcyclohexoxide.



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 in a KBr disk. Naphthalene-d_8, $LiAlD_4$ and cyclohexanol-d_{12} were purchaced from E. Merck, Darmstadt, Germany.

1,2-Benzenedicarboxaldehyde-d_6 (I):

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°; lit. 53.2°; 56-57° for the H analog. Ir, 2130 cm^{-1},CDO; anal. calcd. C,68.55; D,8.62; found C,68.24; D,8.59;

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.

1,4-Cyclohexanedione-d_8 (II):

1,4-Cyclohexanedione (5 g,45 mmol.) was dissolved in an already reacted mixture of D_2O (30 ml., 1.7 mol.) and PCl_5 (0.5 g, 2.4 mmol.). The solution was stirred 24 hrs at 50°. After cooling, the solid was filtered off and was washed with a small amount D_2O and the same exchange procedure was repeated twice. The degree of exchange was followed by NMR measurements. After the third exchange, the solid was dried and sublimed two times, yielding 4.0 g white solid, m.p. 79.6°, lit. 78-80°. Ir, 2125 cm^{-1},CD_2; 2940 cm^{-1},CH_2 was not found. Anal. calcd. C,29.97; D,13.40; found C,60.01; D,13.24, mass anal. m/e 120,$C_6D_8O_2$; m/e 60,C_4D_6.

6,13-Pentacenequinone-d_{12} (III):

I (0.9 g, 6.4 mmol.) and II (0.36 g, 3 mmol.) were dissolved in abs. ethanol (100 ml.) and heated to 50°, thereafter 10% KOH in D_2O (1.5 ml.) was added to the solution. The mixture was stirred during ½ hr at 50°, cooled, whereafter the solid was filtered off and washed with a small amount of ethanol and recrystallized from N,N dimethylformamide (DMF), yielding 0.71 g yellow needles. Ir, 2290 cm^{-1},CD; 1675 cm^{-1},CO; 2940 and 1680 cm^{-1} for CH and CO in the H analog, both were not found. Anal. calcd. C,82.49; D,7.52; found C,82.16; D,7.68. Mass anal. m/e 320,$C_{22}D_{12}O_2$; m/e 292; 264; m/e 160,$C_{11}D_6O$; m/e 134; 130. Uv, absorbtion max. in benzene, 303 and 402 nm; lit. H analog 300 and 403 nm.

Pentacene-d_{14} (IV):

Aluminum foil (0.05 g, 1.7 mmol.), cyclohexanol-d_{12} (5 ml., 43 mmol.), carbontetrachloride (2.5 mg) and $HgCl_2$ (2.5 mg) were heated under reflux and dry N_2 until the aluminum foil was dissolved. After cooling the mixture, III (0.05 g, 0.16 mmol.) was added under stirring, another 4 hrs refluxed, cooled and thereafter D_2O (5 ml.) and 37% DCl in D_2O (3 ml.) were added. The pentacene was filtered off, was washed with D_2O and dried. Under high vacuum was sublimed, yielding 10 mg deep blue powder. Mass anal. m/e 292, $C_{22}D_{14}$; m/e 146,$C_{11}D_7$. Uv, absorbtion max. in pyridine, 495, 534 and 580 nm; lit. 495, 534 and 580 nm for the H analog.

Pentacene 1,2,3,4,5,7,8,9,10,11,12,14-d_{12} (V):

Aluminum foil (0.116 g, 4.3 mmol.), cyclohexanol (5 ml., 48 mmol.), carbontetrachloride (0.05 g) and $HgCl_2$ (3 mg) were heated under reflux and dry N_2 until the aluminum foil was dissolved. After cooling the mixture, III (0.116 g, 0.36 mmol.) was added and then for 16 hrs heated at 200°. The mixture was then cooled water (5 ml.) and 37% HCl (3 ml.) were added, further diluted with water (95 ml.) and the blue mixture filtered off, washed with water and ethanol and dried. The powder was sublimed under high vacuum, yielding 40 mg deep blue product. Ir, 3060 cm^{-1},CH; 2280 cm^{-1},CD. Mass anal. m/e 290,$C_{22}D_{12}H_2$; m/e 145,$C_{11}D_6H$. Uv, absorbtion max. in pyridine, gave the same spectrum as IV.

1,2-Benzenedicarboxaldehyde-d_2 (VI):

IX (4.0 g, 27.8 mmol.) and SeO_2 (3.2 g, 28.8 mmol.) were slowly heated to 150° and the water was distilled off. The dry residue was heated in a bulb-to-bulb distillation apparatus above 200°, the distilled product was taken up in diethyl ether and was dried. The solvent was removed and the residue was sublimed, yielding 1.4 g light-yellow crystals. M.p. 55.0°; lit. 53.2°; 56-57° for the H analog. Ir, 2130 cm^{-1},CDO; 1675 cm^{-1},CO. Mass anal. m/e 136,$C_8H_4D_2O_2$; m/e 106,C_7H_4DO; m/e 78,C_6H_4D; m/e 51,C_4H_3; a small amount of m/e 148,$C_8H_4O_3$ was also found.

6,13-Pentacenequinone 5,7,12,14-d_4 (VII):

VI (1 g, 7.4 mmol.) and II (0.4 g, 3.3 mmol.) were dissolved in abs. ethanol (125 ml.) and heated to 50-60° and thereafter 10% KOH in water (1.5 ml.) was added to the solution. The mixture was stirred 1 hr at 60°, cooled and the solid was filtered off, washed with ethanol and recrystallized from hot DMF. The fine yellow needles so obtained were washed with diethyl ether and dried, yielding 0.83 g. Ir, 3070 cm^{-1},CH; the CD peak was not visible; 1675 cm^{-1},CO. Uv, absorbtion max. in benzene, 302.5 and 402 nm, see also the uv spectra of compound III. Mass anal. m/e 312,$C_{22}D_4H_8O_2$; m/e 284; 256; m/e 156,$C_{11}D_2H_4O$; m/e 128 and m/e 127.

Pentacene 5,7,12,14-d_4 (VIII):

Aluminum foil (0.09 g, 3.3 mmol.), cyclohexanol (1.8 ml., 17.3 mmol.), bromine (0.01 g) were heated at 200° under dry N_2. The reaction was very slow and after

24 hrs there was still aluminum foil left. Then there was added $HgCl_2$ (0.01 g), whereafter the reaction started. After all the aluminum foil had dissolved, the mixture was cooled and VII (0.09 g, 0.3 mmol.) was added. The blue mixture was heated during 48 hrs at 200^o, cooled, the product was filtered off, washed with water and benzene and dried. The blue product was sublimed under high vacuum, yielding 25 mg deep blue powder. Ir, 3060 cm^{-1},CH; 2280 cm^{-1},CD; 1675 cm^{-1},CO was missing. Uv, absorbtion max. in pyridine, as product IV. Mass anal. m/e 282,$C_{22}D_4H_{10}$; m/e 281,$C_{22}D_3H_{11}$; m/e 280,$C_{22}D_2H_{12}$; m/e 279,$C_{22}DH_{13}$; m/e 278,$C_{22}H_{14}$; all five derivatives in roughly 20% concentration; m/e 141,$C_{11}D_2H_5$; m/e 140, $C_{11}DH_6$; m/e 139,$C_{11}H_7$, all three derivatives in roughly 33% concentration.

1,2-Bis(hydroxymethyl-d_3) benzene (IX):

1,2-Benzenedicarboxylic acid dimethylester (10 g, 52 mmol.) in diethyl ether (250 ml.) and tetrahydrofuran (50 ml.) (all three chemicals dried before usage) was reduced with $LiAlD_4$ (2.65 g, 63 mmol.), refluxed 1 hr and left overnight at roomtemperature. The mixture was cooled at 0^o, whereafter D_2O (2.6 ml.), 15% NaOH in D_2O (2.6 ml.) and D_2O (7.5 ml.) were added in this order. (By this method(8) a dry granular precipitate was obtained.) The precipitate was filtered off, washed with diethyl ether, the upper layer was separated, dried, filtered and the solvent removed. After distillation of the residue, b.p. 120^o/0.01 mm, 4.3 g white solid was obtained, m. p. 63.2^o, lit. $64.2-64.8^o$ for the H analog. Ir, 1735 cm^{-1},CO was missing. Without further purification this was used for the preparation of 1,2-benzenedicarboxaldehyde-d_2 (VI).

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REFERENCES

1. Brown W.G. and Garnett J.L. -J. Amer. Chem. Soc. 80: 5272 (1958)
2. Garnett J.L., Long M.A., Vining R.F.W. and Mole T. -J. Amer. Chem. Soc. 94: 5913 (1972)
3. Ried W. und Anthöfer F. -Angew. Chem. 65: 601 (1953)
4. B.H. Kwant, previous article in this journal.
5. Wood G., Woo E.P. and Miskow M.H. -Can. J. of Chem. 47: 429 (1969)
7. Bruckner V. und Tomasz J. -Acta Chim. Hung. Tomus 28: 405 (1961)
6. Bruckner V., Karczag (Wilhelms) A., Körmendy K., Meszaros M. und Tomasz J.- Tetrahedron Letters 1: 5 (1960)
8. Mićović V.M. and Mihailović M. LJ. -J. Org. Chem. 18: 1190 (1953)