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Rearrangement of 11-Hydroxy-11-(2-naphthyl)-3,4:8,9-dibenzobicyclo [4.4.1]undeca-3,8-diene-2,2,5,5,7,7,10,10-d_8

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Rearrangement of 11-Hydroxy-11-(2-naphthyl)-3,4:8,9-dibenzobicyclo[4.4.1]undeca-3,8-diene-2,2,5,5,7,7,10,10-d_8

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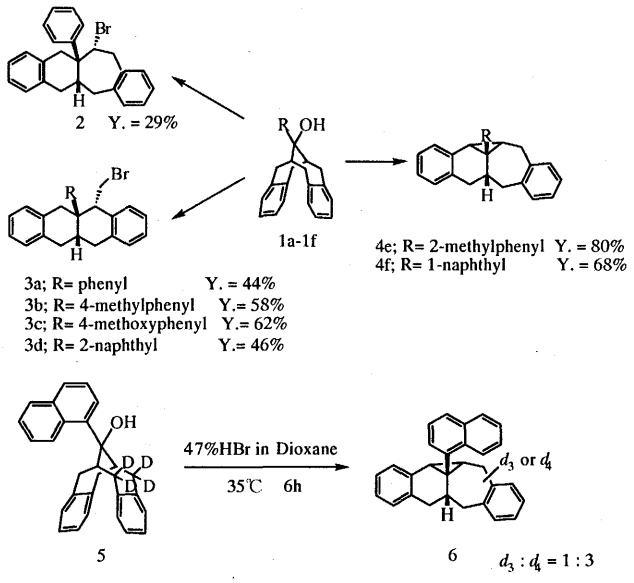
The preparation of a novel deuterated [3.3]orthocyclophane-alcohol is described. The rearrangement of the orthocyclophane alcohol leads to a dibenzo-annelated bromomethyldecaline. The deuterium labels provide a good indication of the mechanism that is underlying this reaction.

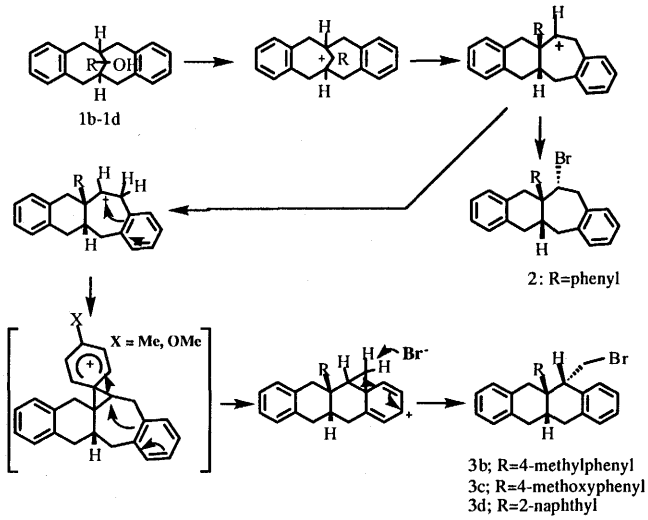
Introduction

[3.3]Orthocyclophanes with rigid, layered structures show interesting properties due to their closely layered π-systems[1-5] and due to their strain within their bridging [4.4.1]undecane subunit. Recently, it has been reported that the treatment of orthocyclophane-alcohols **1** with hydrobromic acid in dioxane, produced rearrangement products, the nature of which is dependent on the aryl substituent on the bridge of **1**.



Scheme 1

In the rearrangement of 1-naphthyl and 2-methylphenyl-substituted orthocyclophane-alcohols **1e** and **1f**, a cyclopropane-ring was formed, giving product **4e** and **4f**. From the study on the rearrangement of deuterated 1-naphthyl[3.3]orthocyclophane-alcohol **5**-d_4, it was deduced that the cyclopropane ring is formed via a non-classical cation derived from a tertiary cation, which has a chair-chair conformation due to the bulky substituent.[6] Phenyl-substituted orthocyclophane-alcohol **1a** gave two rearrangement products, **2** and **3a** (Scheme1).



Scheme 2

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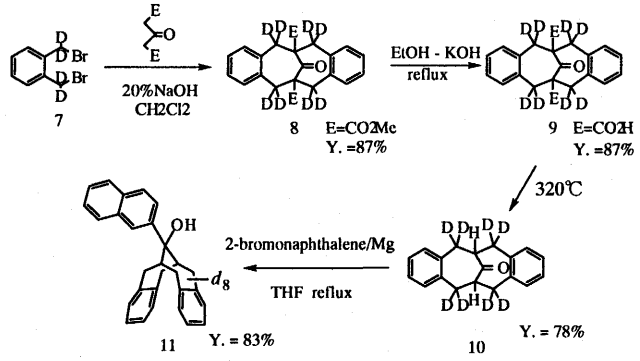
On the other hand, **3b-c** are the sole products in the rearrangement of orthocyclophane-alcohols **1b-c**, which possess an electron-rich aryl group. The formation of **2** can be explained by a Wagner-Meerwein type rearrangement of the cation generated and the rearrangement giving **3a-3d** is assumed to proceed via a phenonium ion, which is especially favorable for an electron-rich aryl group (Scheme 2).

In the present paper, carbinol **11**-d_8, bridge-methylene protons of which have all been substituted by deuterium atoms, was prepared and its rearrangement was carried out in order to ascertain the pathway leading to the formation of the bromomethyl group in **3a-3d**.

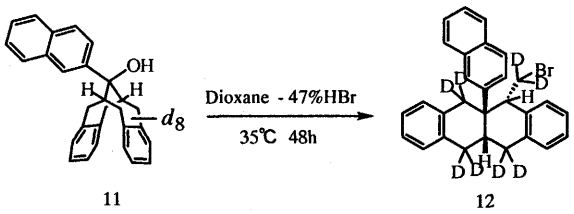
Results and Discussion

Dibenzobicyclo[4.4.1]undeca-11-one-d_8 **10** can easily be prepared as follows: 1,2-Bis(bromomethy)lbenzene-d_4 (**7**) of high isotopic purity (> 99%) is prepared, according to the procedure reported. [6] The reaction of **7**-d_4 with dimethyl acetonedicarboxylate under phase transfer conditions in the presence of a strong base gives dibenzobicyclo[4.4.1]undecadienes **8**-d_8. A subsequent hydrolysis of the diester **8**-d_8 and decarboxylation of the corresponding dicarboxylic acid **9**-d_8 yields diketone **10**-d_8. Diketone **10**-d_8 can be transformed to 2-naphthyl carbinol **11**-d_8 by Grignard reaction as has been described previously for the non-deuterated compounds (Scheme 3).



Scheme 3

The two remaining protons on the bridge-head positions in **11**-d_8 were ascertained by ^{1}H- and ^{13}C-NMR (Scheme 4). The deuterium contents (>99%) of the intermediates **8-11**-d_8 were determined by mass spectroscopy.



Scheme 4

Carbinol **11**-d_8 was treated with hydrobromic acid in dioxane at 35 ℃ for 48h and the rearrangement product **12**-d_8 was obtained in 83% yield. The ^{1}H-NMR spectrum of **12**-d_8 shows two singlets at δ 2.89 and 3.93 ppm, respectively, each of an equal intensity. In the ^{13}C-NMR spectrum three singlet signals are observed at δ 37.74, 45.89, and 51.88 ppm. By analyzing the ^{1}H- and ^{13}C-signals of the aliphatic region of **12**, the two protons of the rearrangement product **12**-d_8 can be assigned to that bridge-carbon of the decaline system, which is located on the side opposite to the bromomethyl-unit and the benzylic carbon which carries the bromomethyl group itself.

These findings can be reasonably explained by the proposed mechanism for the rearrangement of **11** to **12**.

Experimental

Melting points were measured on a Yanaco micro melting point apparatus and are uncorrected. Infrared spectra were measured with JASCO IR-700 and Nippon Denshi JIR-AQ2OM machines. ^{1}H- and ^{13}C-NMR spectra were recorded with a JEOL EX-270 spectrometer. The chemical shifts are relative to TMS (solvent CD_2Cl_2). Mass spectra were measured with a JMS-01-SG-2 spectrometer (EI, 70 eV).

Diester **8**-d_8

To a stirred mixture of tetrabutylammonium bromide (8.10 g, 25 mmol), CH_2Cl_2 (16 mL) and 23% aq. NaOH (20 mL) was added dropwise a solution of 1,2-bis(bromomethyl)benzene-d_4 **7**-d_4[8] (2.20 g, 8.0 mmol) and dimethyl acetone-1,3-dicarboxylate (2.50 g, 14 mmol) in CH_2Cl_2 (15 mL). The resulting two-phase system was stirred for 24 h at rt. Thereafter the phases were separated, the organic phase was washed with water (2 x 50 mL) and dried over anhydrous Na_2SO_4. After concentration of the solution *in vacuo*, the residue was taken up in methanol to give **8**-d_8 (7.26g, 87%) as colorless prisms, mp 182-184 ℃ (Found M^+ 386.1964. $C_{23}H_{14}D_8O_5$ requires *M*, 386.1969); ν_{max} (KBr)/cm^{-1} 2956, 1795, 1674, 1450, 1278, 1230, 747; *m/z* (EI) 386 (M^+).

Dicarboxylic acid **9**-d_8

To a solution of **8**-d_8 (1.57 g, 4.1 mmol) in ethanol (80 mL) was added KOH (5.70 g, 10 mmol) and the resulting slurry was refluxed for 3h. After the mixture was cooled, it was poured into water (250 mL). The solution was acidified with 35wt % aq. HCl (10 mL) and was kept at rt for 14h. The precipitate formed was filtered to give **9**-d_8 (1.30 g, 90%) as a colorless solid, mp 330℃ (decomp); (Found M^+ 358.1655. $C_{21}H_{10}D_8O_5$ requires *M*, 358.1656); ν_{max} (KBr)/cm^{-1} 3600, 3031, 1740, 1442, 1217 and 747; *m/z* (EI) 358 (M^+).

Ketone **10**-d_8

Dicarboxylic acid **9**-d_8 (1.20 g, 3.35 mmol) was heated *in vacuo* (0.2-0.4 torr) at 320℃ until the gas evolution ceased. After the reaction mixture was cooled, it was dissolved in CH_2Cl_2 (20 mL). Insoluble material was filtered off. The filtrate was concentrated *in vacuo* and submitted to a column chromatography on silica gel (chloroform) to give **10**-d_8 (700 mg, 78%) as a colorless solid, mp 132-133° C (Found M^+ 270.1859. $C_{19}H_{10}D_8O$ requires *M*, 270.1860); ν_{max} (KBr)/cm^{-1} 3041, 1733, 1434, 1219, 771; *m/z* (EI) 270 (M^+).

Carbinol **10**-d_8

Ketone **10**-d_8 (0.30 g, 1.1 mmol) in dry THF (5 mL) was added dropwise within 1h to the Grignard reagent, prepared from 2-bromonaphthalene (0.43 g, 2.1 mmol) and Mg (0.14 g, 5.2 mmol) in THF (5 mL). The mixture was heated under reflux for 15h. After cooling, a 17 wt% aq. NH_4Cl solution (30 mL) was added. The phases were separated, the aqueous phase was extracted with ether (2 X 50 mL) and the combined phases were dried over anhydrous $MgSO_4$. After evaporation *in vacuo*, the crude material was subjected to column chromatography on silica gel (toluene) to yield **11**-d_8 (0.37g, 83%) as a colorless solid, mp 241-243 ℃ (Found M^+ 398.2487. $C_{29}H_{18}D_8O$ requires *M*, 398.2486); ν_{max} (KBr)/cm^{-1} 3546, 3056, 1493, 1181 and 760; 1H NMR (270 MHz, CD_2Cl_2) δ = 1.72 (1H, s), 3.34 (2H, s), 6.44 - 6.88 (7H, m), 7.44 - 7.48 (2H, m), 7.79 - 7.84 (5H, m), 8.00 (1H, s); ^{13}C NMR (67.8 MHz) δ = 39.42, 79.19, 124.09, 125.35, 125.82, 126.07, 126.22, 127.34, 128.35, 129.76, 130.42, 132.25, 133.12, 138.97, 139.84, 143.16; *m/z* (EI) 398 (M^+).

Rearrangement of **11**-d_8

To **11**-d_8 (0.20 g, 0.51 mmol) in dioxane (21 mL) was added dropwise 47%wt aq. HBr (50 mL) and the reaction mixture was stirred for 48h at rt. Then, the phases were separated. The organic phase was washed with water (50 mL) and dried over anhydrous Na_2SO_4. After concentration of the solution *in vacuo*, the resulting residue was recrystallized from benzene to give **12**-d_8 (0.19 g, 83%) as a colorless solid, mp 180-186℃ (decomp.); (Found M^+ 460.1643. $C_{29}H_{17}D_8[^{79}Br]$. $C_{29}H_{17}D_8[^{79}Br]$ requires *M*, 460.1642); ν_{max} (KBr)/cm^{-1} 2926, 1488, 1451, 1120, 1036 and 751; ^1H NMR (270MHz, CD_2Cl_2) δ = 2.89 (1H, s), 3.93 (1H, s), 6.63-7.87 (15H, m); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ = 37.74,

45.89, 51.88, 124.85, 125.64, 126.23, 126.29, 126.41, 126.45, 126.56, 126.68, 126.86, 127.10, 127.51, 127.67, 127.96, 128.32, 128.55, 128.93, 129.25, 129.36, 129.47, 129.86, 130.31, 132.52, 133.55, 134.70, 135.18, 136.39, 136.48, 142.55; *m/z* (EI) 460 ([^{79}Br]M^{+}) and 462 ([^{81}Br]M^{+}).

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