

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-d₈

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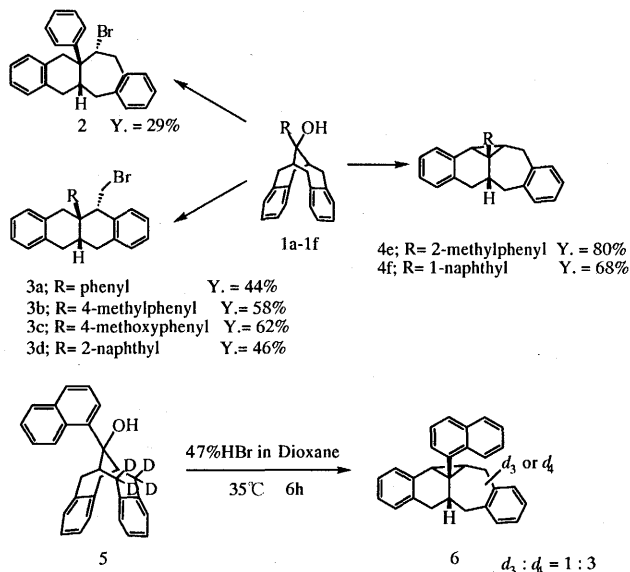
Rearrangement of 11-Hydroxy-11-(2-naphthyl)-3,4:8,9-dibenzobicyclo[4.4.1]undeca-3,8-diene-2,2,5,5,7,7,10,10-*d*₈

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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.

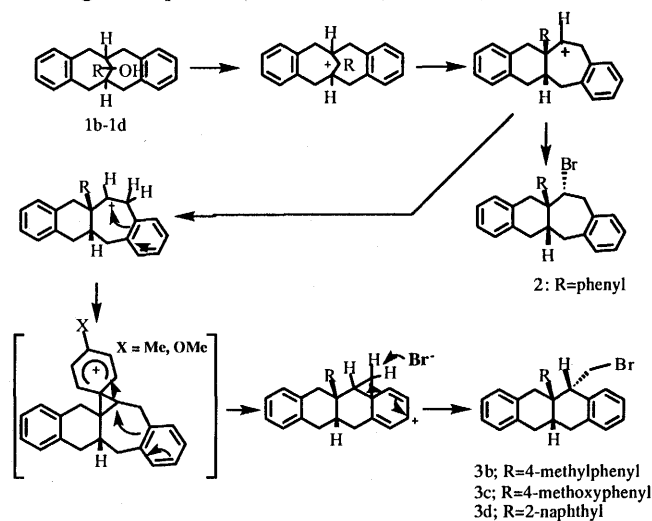
Introduction

[3.3]Orthocyclophanes with rigid, layered structures show interesting properties due to their closely layered π -systems¹⁻⁵⁾ 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-d₈**, 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** (Scheme 1).



Scheme 2

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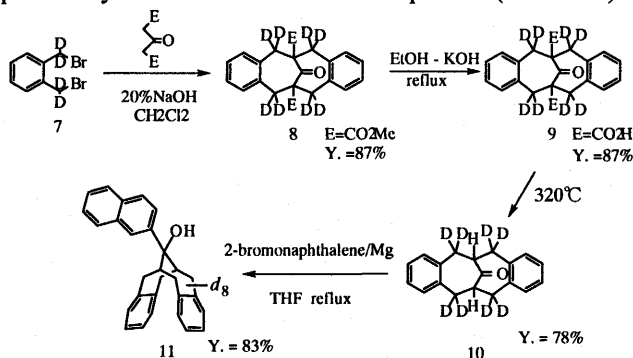
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On the other hand, **3b-c** are the sole products in the rearrangement of orthocyclophane-alcohols **1b-c**, which possess an electron-rich aryl group. The formation of **2** can be explained by a Wagner-Meerwein type rearrangement of the cation generated 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-d₈**, 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**.

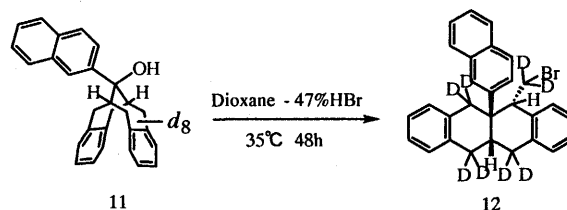
Results and Discussion

Dibenzobicyclo[4.4.1]undeca-11-one-d₈ **10** can easily be prepared as follows: 1,2-Bis(bromomethyl)benzene-d₄ (**7**) of high isotopic purity (> 99%) is prepared, according to the procedure reported.⁶⁾ The reaction of **7-d₄** with dimethyl acetonedicarboxylate under phase transfer conditions in the presence of a strong base gives dibenzobicyclo[4.4.1]undecadienes **8-d₈**. A subsequent hydrolysis of the diester **8-d₈** and decarboxylation of the corresponding dicarboxylic acid **9-d₈** yields diketone **10-d₈**. Diketone **10-d₈** can be transformed to 2-naphthyl carbinol **11-d₈** 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-d₈** were ascertained by ¹H- and ¹³C-NMR (Scheme 4). The deuterium contents (>99%) of the intermediates **8-11-d₈** were determined by mass spectroscopy.



Scheme 4

Carbinol **11-d₈** was treated with hydrobromic acid in dioxane at 35 °C for 48h and the rearrangement product **12-d₈** was obtained in 83% yield. The ¹H-NMR spectrum of **12-d₈** shows two singlets at δ 2.89 and 3.93 ppm, respectively, each of an equal intensity. In the ¹³C-NMR spectrum three singlet signals are observed at δ 37.74, 45.89, and 51.88 ppm. By analyzing the ¹H- and ¹³C-signals of the aliphatic region of **12**, the two protons of the rearrangement product **12-d₈** 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-AQ20M machines. ¹H- and ¹³C-NMR spectra were recorded with a JEOL EX-270 spectrometer. The chemical shifts are relative to TMS (solvent CD₂Cl₂). Mass spectra were measured with a JMS-01-SG-2 spectrometer (EI, 70 eV).

Diester 8-d₈

To a stirred mixture of tetrabutylammonium bromide (8.10 g, 25 mmol), CH₂Cl₂ (16 mL) and 23% aq. NaOH (20 mL) was added dropwise a solution of 1,2-bis(bromomethyl)benzene-d₄ 7-d₄⁸⁾ (2.20 g, 8.0 mmol) and dimethyl acetone-1,3-dicarboxylate (2.50 g, 14 mmol) in CH₂Cl₂ (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 Na₂SO₄. After concentration of the solution *in vacuo*, the residue was taken up in methanol to give 8-d₈ (7.26g, 87%) as colorless prisms, mp 182-184 °C (Found M⁺ 386.1964. C₂₃H₁₄D₈O₅ requires M, 386.1969); ν_{max} (KBr)/cm⁻¹ 2956, 1795, 1674, 1450, 1278, 1230, 747; m/z (EI) 386 (M⁺).

Dicarboxylic acid 9-d₈

To a solution of 8-d₈ (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-d₈ (1.30 g, 90%) as a colorless solid, mp 330 °C (decomp); (Found M⁺ 358.1655. C₂₁H₁₀D₈O₅ requires M, 358.1656); ν_{max} (KBr)/cm⁻¹ 3600, 3031, 1740, 1442, 1217 and 747; m/z (EI) 358 (M⁺).

Ketone 10-d₈

Dicarboxylic acid 9-d₈ (1.20 g, 3.35 mmol) was heated *in vacuo* (0.2-0.4 torr) at 320°C until the gas evolution ceased. After the reaction mixture was cooled, it was dissolved in CH₂Cl₂ (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-d₈ (700 mg, 78%) as a colorless solid, mp 132-133 °C (Found M⁺ 270.1859. C₁₉H₁₀D₈O requires M, 270.1860); ν_{max} (KBr)/cm⁻¹ 3041, 1733, 1434,

1219, 771; m/z (EI) 270 (M⁺).

Carbinol 10-d₈

Ketone 10-d₈ (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. NH₄Cl 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 MgSO₄. After evaporation *in vacuo*, the crude material was subjected to column chromatography on silica gel (toluene) to yield 11-d₈ (0.37g, 83%) as a colorless solid, mp 241-243 °C (Found M⁺ 398.2487. C₂₉H₁₈D₈O requires M, 398.2486); ν_{max} (KBr)/cm⁻¹ 3546, 3056, 1493, 1181 and 760; ¹H NMR (270 MHz, CD₂Cl₂) 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); ¹³C 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-d₈

To 11-d₈ (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 Na₂SO₄. After concentration of the solution *in vacuo*, the resulting residue was recrystallized from benzene to give 12-d₈ (0.19 g, 83%) as a colorless solid, mp 180-186 °C (decomp.); (Found M⁺ 460.1643. C₂₉H₁₇D₈[⁷⁹Br]. C₂₉H₁₇D₈[⁷⁹Br] requires M, 460.1642); ν_{max} (KBr)/cm⁻¹ 2926, 1488, 1451, 1120, 1036 and 751; ¹H NMR (270MHz, CD₂Cl₂) δ = 2.89 (1H, s), 3.93 (1H, s), 6.63-7.87 (15H, m); ¹³C NMR (67.8 MHz, CDCl₃) 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 ($[^{79}\text{Br}]\text{M}^+$) and 462 ($[^{81}\text{Br}]\text{M}^+$).

References

- 1) S. Mataka, K. Takahashi, T. Hirota, K. Takuma, H. Kobayashi, and M. Tashiro, *J. Chem. Soc., Chem. Commun.*, **1985**, 973-973.
- 2) S. Mataka, K. Takahashi, T. Mimura, T. Hirota, K. Takuma, H. Kobayashi, M. Tashiro, K. Imada, and M. Kuniyoshi, *J. Org. Chem.* **1987**, *52*, 2653-2656.
- 3) S. Mataka, Y. Mitoma, T. Sawada, and M. Tashiro, *Tetrahedron Lett.* **1996**, *37*, 65-68.
- 4) S. Mataka, Y. Mitoma, T. Thiemann, T. Sawada, M. Taniguchi, M. Kobuchi, and M. Tashiro, *Tetrahedron* **1997**, *53*, 3015-3026.
- 5) (a) S. Mataka, K. Shigaki, T. Sawada, Y. Mitoma, M. Taniguchi, T. Thiemann, K. Ohga, and N. Egashira, *Angew. Chem.* **1998**, *110*, 2626 - 2628; *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 2532-2534. (b) M. Taniguchi, S. Mataka, T. Thiemann, T. Sawada, K. Mimura, and Y. Mitoma, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2661-2668. (c) S. Mataka, J. Ma, T. Thiemann, J. M. Rudzinski, H. Tsuzuki, T. Sawada, and M. Tashiro, *Tetrahedron* **1997**, *53*, 885-902.
- 6) S. Isobe, M. Taniguchi, T. Sawada, T. Thiemann, T. Yonemitsu, and S. Mataka, *J. Chem. Soc., Perkin Trans. I*, **1999**, 2102-2107.
- 7) M. Brock, H. Hintze, and A. Heesing, *Chem. Ber.*, **1986**, *119*, 3718.