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An Improved Synthesis of Trisnaphtho[3.3.3]propellane

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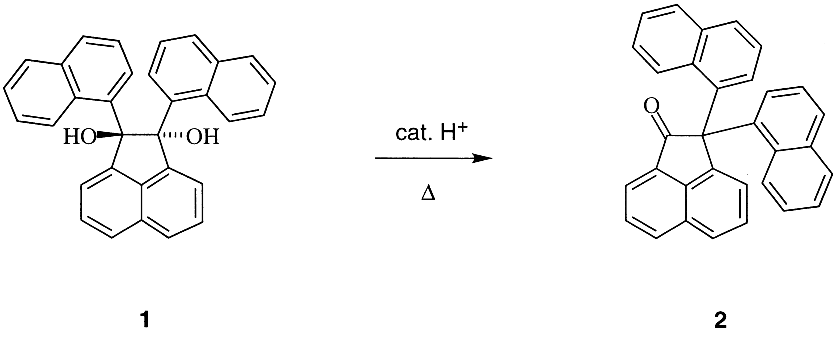
Abstract—The strained propellane **5** is efficiently synthesized from **3** in three reaction steps including epoxidation, organometallic arylation and final cyclization by intramolecular Friedel–Crafts alkylation. © 2000 Elsevier Science Ltd. All rights reserved.

In 1990 Alder and co-workers[1] reported on an attempt to synthesize the highly symmetric trisnaphtho[3.3.3]propellane **5** from pinacol **1** under various acidic conditions, similar to the successful synthesis of related [4.4.4]- and [4.4.3]propellanes by Wittig and Schoch[2] or the synthesis of tribenzo[3.3.3]propellanes by Kuck and coworkers.[3] In this case the rearrangement stopped at the stage of the pinacolone **2**, which refused to cyclize. Recently we found that the strained ring system **5** can be obtained by a palladium-catalyzed annulation reaction of hexacycle **3** with 1-iodonaphthalene **4**.[4] This Heck-type coupling process is also suitable for the efficient construction of [4.3.3]propellanes by applying substituted iodobenzenes as coupling components. However, since iodonaphthalene **4** reacts rather sluggishly this straightforward synthesis of **5** has some major disadvantages: the required reaction time exceeds two weeks and a large excess of **4** has to be applied, leading to a large amount of 1,1′-binaphthyl as by-product. Therefore the separation of **5** is somewhat tedious, and we have developed an independent and superior pathway (Schemes 1 and 2): for the epoxidation of **4** under neutral conditions dimethyldioxirane (**6**) is applied;[5] according to our own results, ring opening of the epoxide **7** takes place even under only slightly acidic conditions. For instance, epoxidation of **3** with *m*-chloroperbenzoic acid results in the addition of the corresponding benzoic acid to the intermediary epoxide **7** even in the presence of excess base (resulting in the formation of a β-hydroxy benzoate). **7** is not stable under the conditions of a column chromatography on silica, but can be easily purified by recrystallization from dichloromethane/*n*-pentane. The X-ray crystal structure analysis[6] reveals an elongation of the central single bond C6b-C12b to 149.4(2) pm compared to the typical 147.2 pm for simple oxiranes. The bridgehead carbon atoms are only slightly pyramidalized:[7] the carbon atom C6b is only 12.1 pm out of the plane defined by the neighboring atoms C6a, C6c and O1. The interplanar angle between the two naphthyl groups (including C6b and C12b) is 35° (Fig. 1).



Scheme 1. Pinacol rearrangement of **1** according to Alder et al.[1]

Keywords: dimethyldioxirane; epoxidation; Friedel–Crafts alkylation; propellanes.

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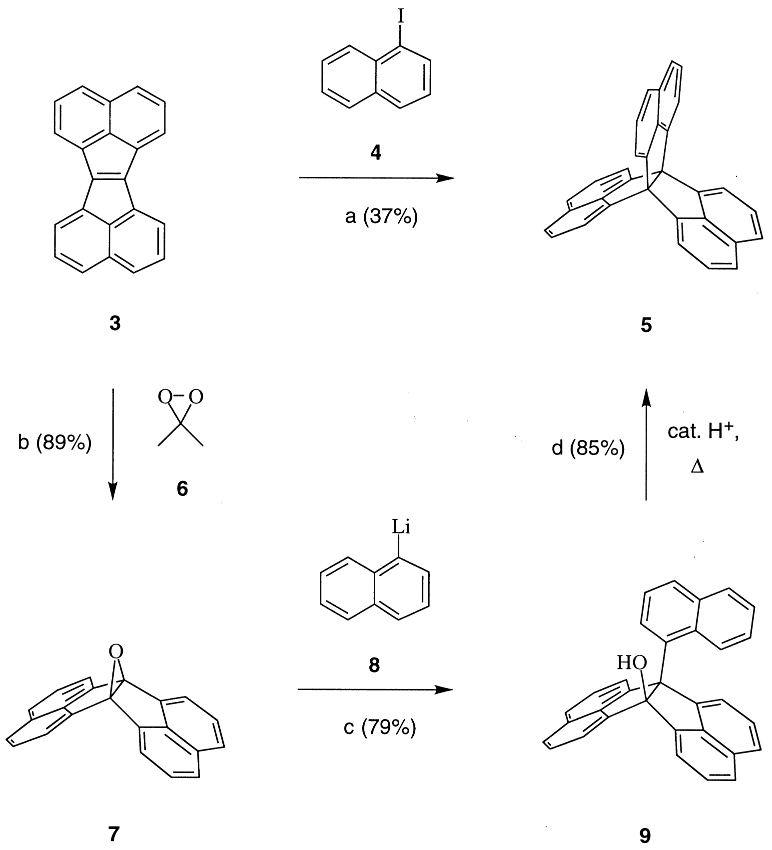


Scheme 2. Independent syntheses of propellane **5**; reaction conditions: (a) 30 equiv. aryl iodide **4**, 5 mol-% $Pd(OAc)_2$, K_2CO_3, *n*-Bu_4NBr, DMF, N_2, 21 days, 100°C; (b) dimethyldioxirane (**6**),[5] acetone, room temperature; (c) excess **8**, diethyl ether, −10°C to room temperature; (d) H_3PO_4, xylene, Dean–Stark trap, 190°C, 48 h.

The third naphthalene unit is introduced by the addition of the organolithium reagent **8** to the epoxide **7**, resulting in the arylation at the benzylic position. The corresponding Grignard reagent, naphthyl magnesium bromide, is less suitable for this reaction step: the ring opening of complex **10** is followed by transfer of the naphthyl group or the bromide to the benzylic position leading to a 1:1.8 mixture of the desired product **9** and the competing product **11** (Scheme 3). The rotation of the naphthyl group of **9** is obviously hindered since in the ^{13}C NMR spectrum the signals of 19 different methine groups are clearly distinguished.

The tertiary alcohol **9** represents a key intermediate of Alder's original plan for the synthesis of **5** (see above) and indeed, **9** cyclizes smoothly under acidic conditions at elevated temperatures (Scheme 2). The overall yield of this three step synthesis is 60% giving convenient access to the strained hydrocarbon **5**, which is of interest for studies concerning the reactivity of the elongated but sterically protected central CC single bond.

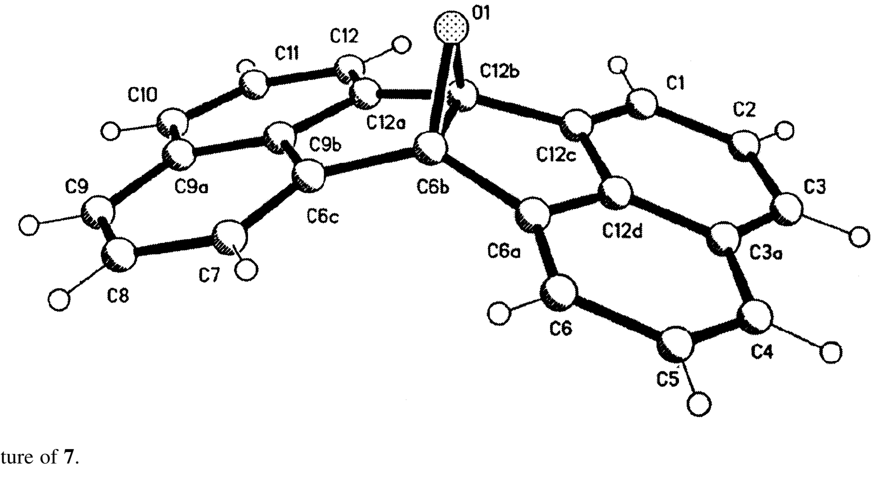
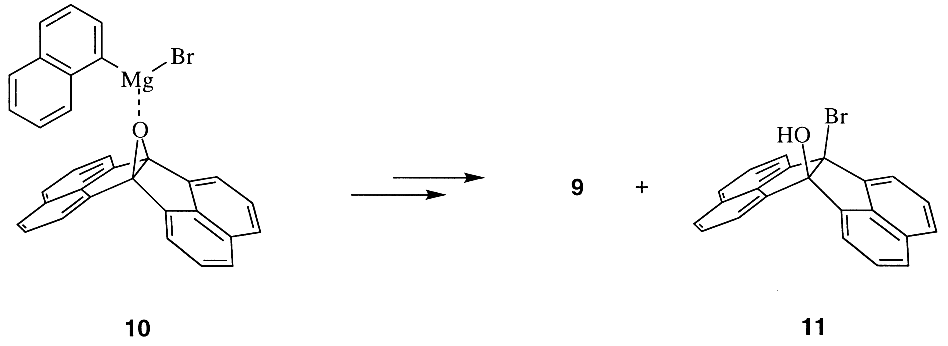


Figure 1. Molecular structure of **7**.



Scheme 3. Modes of ring opening of epoxide **7** by addition of 1-naphthyl magnesium bromide.

Experimental

General

Melting points are uncorrected. IR: Nicolet 320. UV/Vis: HP 8452 A. NMR: Bruker AM 400. ^{1}H NMR spectra were recorded at 400 or 500 MHz by using $CDCl_3$ as the solvent and TMS as the internal standard. ^{13}C NMR spectra were measured at 100.6 MHz by using $CDCl_3$ as the solvent and the internal standard (d=77.05). MS: Finnigan MAT 8430. Mass spectra were recorded at an ionizing voltage of 70 eV by electron impact. For analytical TLC precoated plastic sheets 'POLYGRAM SIL G/UV254' from 'Macherey-Nagel' were used.

13-Oxa-6b,12b-methano-6b,12b-dihydroacenaphth[l,2-a]acenaphthylene (7). A mixture of 1.11 g (4.00 mmol) of hydrocarbon **3**[8] in 50 ml of acetone and 200 ml of an approximately 0.1N solution of dimethyldioxirane[5] in acetone was stirred for 24 h at room temperature. The solvent was evaporated at reduced pressure at room temperature and the residue dissolved in 200 ml of dichloromethane. After washing twice with 50 ml of water the organic layer was dried with magnesium sulfate and evaporated to dryness. Recrystallization from dichloromethane/pentane gives 1.06 g (89%) of **7** as colorless crystals with mp 244–245°C (decomp.). IR (KBr): $\tilde{\nu}$=3049 cm^{-1} (w), 1481 (m), 1417 (m), 1300 (m), 1200 (m), 1108 (m), 972 (w), 788 (s), 748 (m), 642 (w), 558 (w). UV/Vis (acetonitrile): λ_{max} (log ϵ)=214 nm (4.67), 222 (sh, 4.54), 280 (sh, 3.52), 290 (sh, 3.71), 298 (3.87), 310 (3.86), 318 (sh, 3.51). ^{13}C NMR (400 MHz): δ=7.56 (m, 4H), 7.80 ('d', J=8.3 Hz, 4H), 8.01 ('d', J=6.9 Hz, 4H). ^{13}C NMR (100 MHz): δ=76.94 (s, C-6b/C-12b), 123.38 (d), 126.50 (d), 127.37 (d), 132.43 (s), 136.21 (s), 143.16 (s). MS (70 eV); m/z (%): 293 (24), 292 (100, M$^+$), 276 (22), 263 (24), 150 (42), 138 (11), 132 (27), 113 (10). $C_{22}H_{12}O$ (292.34); Calcd C 90.39, H 4.14, found C 90.52, H 4.12.

***cis*-6b-(1-Naphthyl)-12b-hydroxy-6b,12b-dihydroacenaphth[1,2-a]acenaphthylene (9).** 8.28 g of L-bromonaphthalene (40 mmol) were added dropwise to a mixture of 30 ml of a solution of n-butyllithium in hexane (48 mmol, 1.6N) and 32 ml of diethyl ether at -20°C within 5 min. After stirring for 15 min at +10°C the white suspension was cooled to -20°C and the solvent was carefully removed from the precipitate with a syringe. The residue was washed three times with 20 ml of n-hexane at -20°C and the remaining 1-lithionaphthalene was suspended in 50 ml of dry diethyl ether at -50°C. After the dropwise addition of a solution of 1.06 g (3.63 mmol) of epoxide **7** in 120 ml of dry diethyl ether the reaction mixture was warmed up to room temperature within 16 h. The reaction mixture was carefully hydrolyzed with 40 ml of water and the water layer extracted three times with 100 ml of diethyl ether. The combined ether layer was reextracted with 100 ml of water, dried with magnesium sulfate and the solvent evaporated. Naphthalene was removed by sublimation in the Kugelrohr oven at 80°C/0.5 mbar. The crude product was purified by flash chromatography (silica/n-hexane/Et_2O, R_f=18) to yield 1.20 g (79%) of **9** as colorless crystals with mp 299–301°C. IR (KBr): $\tilde{\nu}$=3484 cm^{-1} (w), 3350 (m), 3043 (w), 1495 (w), 1397 (w) 1355 (w), 1315 (w), 1226 (w), 1181 (w), 1159 (w), 1134 (w), 1099 (s), 1050 (w), 904 (w), 831 (vm), 779 (s), 764 (m). UV/Vis (acetonitrile): λ_{max} (log ϵ)=214 nm (5.10), 276 (4.12), 286 (4.27), 294 (sh, 4.13), 315 (4.08), 328 (4.09). ^{13}C NMR (500 MHz, $CDCl_3$): δ=2.62 (s, 1H, OH), 6.89 (m, 1H), 7.04 (dd, J=8.8, 0.5 Hz, 1H), 7.14 (dd, J=7.4, 1.2 Hz, 1H), 7.28 (m, 1H), 7.31 (t, J=7.8 Hz, 1H), 7.35 (d, J=6.5 Hz, 1H), 7.42 (dd, J=8.2, 7.0 Hz, 1H), 7.55 (dd, J=7.1, 0.8 Hz, 1H), 7.57–7.62 (m, 3H), 7.67 (d, J=7.7 Hz, 1H), 7.70 (dd, J=8.1, 0.8 Hz, 1H), 7.73 (d, J=7.8 Hz, 1H), 7.77 (d, J=8.4 Hz, 1H), 7.79 (d, $J\approx$8 Hz, 1H), 7.81 (d, $J\approx$8 Hz, 1H), 7.83 (d, J=7.2 Hz, 1H), 7.84 (d, J=6.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ=75.33 (s), 96.91 (s), 119.44 (d), 120.06 (d), 121.50 (d), 123.39 (d), 123.67 (d), 123.79 (d), 124.87 (d), 125.03 (d), 125.05 (d), 125.45 (d), 125.61 (d), 126.79 (d), 128.40 (d), 128.73 (d), 128.81 (d), 128.90 (d), 128.98 (d), 129.07 (d), 130.11 (d), 131.66 (s), 131.84 (s), 133.33 (s), 134.81 (s), 135.38 (s), 135.87 (s), 137.08 (s), 145.57 (s), 145.74 (s), 147.16 (s), 148.74 (s). MS (70 eV): m/z (%)=421 (33), 420 (79, M$^+$), 2 (17), 277 (29), 276 (100), 194 (18), 84 (16), 49 (14). Calcd for $C_{32}H_{20}O$: C 91.40, H 4.79; for $C_{32}H_{20}O$. 1/2 CH_2Cl_2: C 84.32, H 4.57; found C 84.58, H 4.53.

6b,12b-[1,8]Naphthalenoacenaphth[1,2-a]acenaphthylene (5). 200 mg (480 μmol) of tertiary alcohol **9** and 4 ml of H_3PO_4 in 80 ml of xylene were heated at the Dean–Stark trap for two days at 180°C. After cooling to room temperature the reaction mixture was washed with an aqueous sodium carbonate solution and dried with magnesium sulfate. The solvent was evaporated and the residue recrystallized from dichloromethane/pentane: 164 mg (85%) of

[3.3.3]propellane **5** as colorless crystals, its NMR spectra were in accord with published data.[4]

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6. X-Ray data of compound **7** have been deposited at the Cambridge Crystallographic Data Centre (deposition number CCDC-124966). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ (Fax (internat.) +44-1223/336033; e-mail: deposit@ccdc.cam.ac.uk). *Crystal data*: $C_{22}H_{12}O$, M_r=292.32, monoclinic, space group $P2_1/n$, a=870.59(10), b=1479.52(12), c=1105.87(12) pm, β=104.251(8)°, V=1.3806 nm^3, Z=4, D_x=1.406 Mg m^{-3}, μ(MoKα)=0.08 mm^{-1}, T=−100°C. *Data collection*: A colourless prism 0.8×0.4×0.4 mm was used to collect 3432 data (2426 unique) to $2\theta_{max}$ 50° on a Siemens P4 diffractometer. *Structure refinement:* The structure was refined anisotropically on F^2 (program SHELXL-93, G. M. Sheldrick, University of Göttingen). Hydrogen atoms were included using a riding model. The final $wR2$ was 0.091 for 208 parameters, $R1$ 0.036; S=0.97, max. $\Delta\rho$ 165 e nm^{-3}.

7. For the molecular structure of a related [3.3.1]propellane, see: Dyker, G.; Körning, J.; Jones, P. G.; Bubenitschek, P. *J. Chem. Res. (S)* **1997**, 132–133.

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