

This article was downloaded by:

On: 27 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Organic Preparations and Procedures International

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t902189982>

### SYNTHESIS AND CONFORMATIONAL PROPERTIES OF 2,2'-DIHYDROXY-9,9'-BIANTHRYL

M. Ghiaci<sup>a</sup>; Y. Bayat<sup>a</sup>

<sup>a</sup> Department of Chemistry, Isfahan University of Technology, Isfahan, IRAN

**To cite this Article** Ghiaci, M. and Bayat, Y.(1996) 'SYNTHESIS AND CONFORMATIONAL PROPERTIES OF 2,2'-DIHYDROXY-9,9'-BIANTHRYL', *Organic Preparations and Procedures International*, 28: 5, 609 – 612

**To link to this Article:** DOI: 10.1080/00304949609458573

**URL:** <http://dx.doi.org/10.1080/00304949609458573>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## OPPI BRIEFS

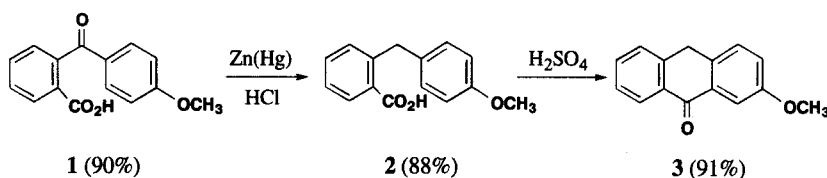
SYNTHESIS AND CONFORMATIONAL PROPERTIES  
OF 2,2'-DIHYDROXY-9,9'-BIANTHRYL

Submitted by M. Ghiaci\* and Y. Bayat  
(11/21/95)

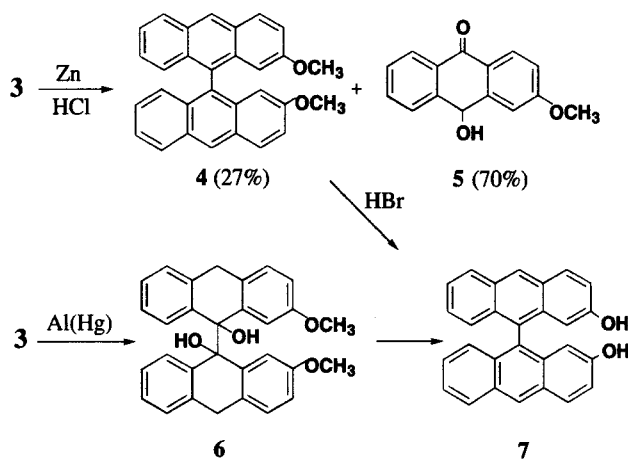
Department of Chemistry  
Isfahan University of Technology, Isfahan 84156, IRAN

In the majority of scenarios for absolute stereochemical control, the presence of a  $C_2$  symmetry axis within the chiral auxiliary can serve the very important function of dramatically reducing the number of possible competing, diastereomeric transition states. A number of workers have noted the importance of this symmetry element in their rational design of chiral auxiliaries. Very early, Noyori<sup>1</sup> utilized 2,2'-dihydroxy-1,1'-binaphthyl as an axially dissymmetric bifunctional molecule.<sup>2</sup> The present article describes a procedure for the synthesis of 2,2'-dihydroxy-9,9'-bianthryl (**7**) as a new biaryl with a  $C_2$  symmetry. Our attempts to test the applicability of **7** in preparing a  $LiAlH_4$  reagent is also reported.

It has been shown<sup>3</sup> that the Clemmensen reduction of 9-anthrone gave a mixture of 9,9'-bianthryl (32%) and anthrapinacol (12%). Thus, 2-methoxy-9-anthrone (**3**), obtained according to the sequence shown below, was refluxed in glacial acetic acid in the presence of zinc powder and hydrochloric acid.

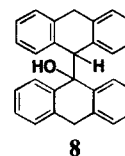


The crude product was chromatographed on silica gel and eluted with *n*-hexane-EtOAc (95:5), to yield 2,2'-dimethoxy-9,9'-bianthryl (**4**) (27%) and 3-methoxy-10-hydroxy-9-anthrone (**5**) (70%), along with 2-methoxy-9,10-dihydroanthracene (2%) as minor product.<sup>4</sup> Treatment of 2,2'-dimethoxy-9,9'-bianthryl (**4**) with conc.  $HBr$ <sup>5</sup> gave **7** in 45% yield; the overall yield of **7** by this route is 8.7%. Reduction of 2-methoxyanthrone (**3**) with aluminum amalgam afforded a 79% yield of 2,2'-dimethoxyanthrapinacol (**6**) which upon dehydration with  $H_2SO_4$  in glacial acetic acid (1:1) under reflux for 7 hrs led to **7** in 95% yield; the overall yield of this route was 54% (from anisole). Although compounds **1** and **2** are known,<sup>9</sup> we describe improved procedures which led to substantially increased yields (Scheme 1).



Scheme 1

An attempt to prepare bianthranylidene by treatment of anthrone with  $\text{TiCl}_4/\text{Zn}$  in THF and pyridine (McMurry reaction),<sup>6</sup> surprisingly gave anthracene (2%), 9,10-dihydroanthracene (10%) and **8** (35%). Compound **8** a colorless solid, mp. 195° was characterized by  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, mass, IR spectroscopy and elemental analysis. Additional evidence for its structure was obtained by extensive decoupling and DEPT experiments. Its  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) showed signals at  $\delta$  6.8-7.4 (m, 16H), 4.4 (s, 1H), 3.15-3.4 (dd, 2H), 2.5 (s, 1H, exchangeable with  $\text{D}_2\text{O}$ ), 2.1 (dd, 2H). On the basis of the MMX force-field,<sup>7</sup> the cyclohexane rings of **8** are in the boat form and the two parts of the molecule are bent in opposite directions. There are four different geminal protons, two of which are in the deshielding zone of the aromatic rings, appearing in the range of  $\delta$  3.15-3.4.



The binaphthol-modified lithium aluminum hydride reagents which have been devised through rational stereochemical engineering, offers promise of asymmetric reduction of carbonyl functions with defined absolute stereochemistry. In this regard we were interested to prepare a new  $\text{LiAlH}_4$  reagent using compound **7**. When  $\text{LiAlH}_4$  was treated with an equimolar amount of **7** in THF under argon atmosphere, the desired complex was not obtained. Force-field calculations by using MMX force-field on compound **7** showed that the approach of the two hydroxyl groups to form internal hydrogen bonding, leads to an increase in the total strain energy of the molecule. We also tried to illustrate the structure of a hypothetical  $\text{LiAlH}_4$  reagent with the compound **7**. PC modeling of the proposed  $\text{LiAlH}_4$  complex shows that the carbon skeleton of the anthranyl rings have to become significantly bent about the carbon atoms of the anthranyl rings. Apparently this increases the total strain energy of the expected complex.

## EXPERIMENTAL SECTION

$^1\text{H}$  NMR spectra were recorded on a Varian EM-390 or a Bruker 400 MHz spectrometers.  $^{13}\text{C}$  NMR spectra were recorded on a 75MHz spectrometer. Melting points were measured on a Kofler hot bench. Infrared spectra were obtained on a Perkin-Elmer FTIR 1600 spectrophotometer.

***o*-(*p*-Anisoyl)benzoic Acid (1).**- A mixture of 100 g (0.68 mole) of phthalic anhydride, 400 mL (3.68 mole) anisole and 240 g (1.8 mole) anhydrous aluminum chloride were heated at 90° for 4 hrs. As soon as the flask was cooled on its own, 200 g of crushed ice was slowly added with shaking. Addition of 150 mL of crude concentrated HCl caused the mass to coagulate and a clear greenish solution was obtained. The unreacted anisole was separated by steam distillation. The resulting solid was dissolved in a previously prepared and heated solution of 50 g of sodium carbonate in 1L of water. The solution was filtered while hot and transferred to a 2L beaker and the acid precipitated by the addition of concentrated HCl to yield *o*-(*p*-anisoyl)benzoic acid (155 g, 90%) as a white solid, mp. 122-123°, lit.<sup>9</sup> 120°. <sup>1</sup>H NMR (90MHz, CDCl<sub>3</sub>): δ 4.2 (s, 3H), 7.2-8.6 (m, 8H), 9.5 (broad singlet, 1H). MS (EI, 20 eV): 256 (M<sup>+</sup>).

*Anal.* Calcd. for C<sup>15</sup>H<sub>12</sub>O<sub>4</sub>: C, 70.31; H, 4.68. Found: C, 70.49; H, 4.75

***o*-(*p*-Methoxybenzyl)benzoic Acid (2).**- In a 500 mL flask was placed 134 g zinc powder, 13.4 g mercuric chloride, 223 mL of distilled water and 6.3 mL concentrated HCl. Occasional agitation during 30 minutes is sufficient for amalgamation. The solution was poured off and the zinc was rinsed once with water. A mixture of 84 mL of water, 196 mL of concentrated hydrochloric acid and 112 mL of toluene and then 80 g *o*-(*p*-anisoyl)benzoic acid was added to the amalgam. The mixture was agitated vigorously until reduction was complete. To the mixture was added 100 mL of Et<sub>2</sub>O, stirring being continued for a few minutes. The organic layer was separated from the aqueous solution and the aqueous layer was extracted with 3x25 mL of Et<sub>2</sub>O. The solution was filtered from suspended matter, and the organic solutions were distilled. The yield of colorless *o*-(*p*-methoxybenzyl)benzoic acid was 88% (66.6 g), mp. 117-118°, lit.<sup>9</sup> 116°. <sup>1</sup>H NMR (90MHz, CDCl<sub>3</sub>): δ 3.8 (s, 3H), 4.5 (s, 2H), 6.8-8.3 (m, 8H). MS (EI, 20eV): 242 (M<sup>+</sup>).

*Anal.* Calcd. for C<sub>15</sub>H<sub>14</sub>O<sub>3</sub>: C, 74.45; H, 5.82. Found: C, 74.72; H, 5.98

**2-Methoxy-9-anthrone (3).**- To 23 mL of concentrated H<sub>2</sub>SO<sub>4</sub> cooled to 0-5° was gradually added (3 hrs) 5 g (0.02 mole) *o*-(*p*-methoxybenzyl)benzoic acid with stirring; the temperature of the reaction mixture was held between 0-5°. The reaction mixture was poured on 200 g crushed ice and 2-methoxy-9-anthrone was collected. The solid residue was recrystallized from toluene. The yield of purified product, mp. 96-97°, was 3.28 g (71%). <sup>1</sup>H NMR (90MHz, CDCl<sub>3</sub>): δ 4.2 (s, 3H), 4.7 (s, 2H), 7.7-9.1 (m, 7H). MS (EI, 20eV): 224 (M<sup>+</sup>).

*Anal.* Calcd for C<sub>15</sub>H<sub>12</sub>O<sub>2</sub>: C, 80.35; H, 5.35. Found: C, 80.46; H, 5.50

**2,2'-Dimethoxyanthrapinacol (6).**- In a 50mL flask fitted with a reflux condenser were placed 9 mL dry benzene, 3.6 mL absolute ethanol, 0.7 g 2-methoxy-9-anthrone (3), and 0.5 g amalgamated aluminum turning. The reaction mixture was heated to boiling on a steam bath for 9 hrs. After cooling, the benzene solution was decanted from a small amount of tarry material and washed with water. After drying over MgSO<sub>4</sub>, the benzene and ethanol were distilled off. The solid residue obtained by evaporation of the solvent, was recrystallized from benzene-petroleum ether (v:v, 60:40) to yield 2,2'-dimethoxy anthrapinacol (0.56 g, 79%), mp. 181°. IR (KBr): 3400 cm<sup>-1</sup> (O-H), 1600, 1499, 1470 cm<sup>-1</sup> (C=C ring stretching). <sup>1</sup>H NMR (90MHz, CDCl<sub>3</sub>): δ 1.7 (s, 2H), 2.1 (d, 2H), 3.6 (d, 2H), 3.8 (s, 6H),

6.9-8.5 (m,4H). MS (EI, 20eV): 450 ( $M^+$ ).

*Anal.* Calcd. for  $C_{30}H_{26}O_4$ : C, 80.00; H, 5.77. Found: C, 80.12; H, 5.81

**2,2'-Dihydroxy-9,9-bianthryl (7).**- A mixture of 2,2'-dimethoxy anthrapinacol (8.5 g, 0.02 mole), acetic acid (150 mL) and concentrated  $H_2SO_4$  (30 mL) was stirred at  $75^\circ$  for 7 hrs and then allowed to cool to  $20^\circ$  and diluted carefully with 100 mL of  $H_2O$ . The greenish solid was chromatographed on  $SiO_2$  (eluent EtOAc-cyclohexane, 10:90) to afford 2,2'-dihydroxy-9,9'-dianthryl (6.9 g, 95%) as a light green crystalline solid, mp.  $280-281^\circ$ .  $^1H$  NMR (400MHz,  $CD_3OD$ ):  $\delta$  6.3 (s, 2H); 6.9-7.15 (m, 4H); 7.25-7.4 (m, 2H); 8.0-8.15 (dd, 4H); 8.6 (s, 2H). MS (EI, 20eV): 386 ( $M^+$ ).

*Anal.* Calcd. for  $C_{28}H_{18}O_2$ : C, 87.04; H, 4.66. Found: C, 87.24; H, 4.81

**Compound 8.**-  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  6.8-7.4 (m, 16H), 4.4 (s, 1H), 3.15-3.4 (dd, 2H), 2.5 (s, 1H, exchangeable with  $D_2O$ ), 2.1 (dd, 2H). MS (EI, 20 eV): 374 ( $M^+$ ).

*Anal.* Calcd. for  $C_{28}H_{22}O$ : C, 89.84; H, 5.88. Found: C, 89.89; H, 5.83

**Acknowledgment.**- We thank the Isfahan University of Technology for partial support of this research.

#### REFERENCES

1. a) R. Noyori, I. Tomino and Y. Tanimoto, *J. Am. Chem. Soc.*, **101**, 3129 (1979); b) R. Noyori, I. Tomino, M. Yamada and M. Nishizawa, *ibid.*, **106**, 6717 (1984).
2. R. Noyori, I. Tomino, Y. Tanimoto and M. Nishizawa, *ibid.*, **106**, 6709 (1984).
3. K. Sunil, C. Syamal and K. Asok, *Tetrahedron*, **46**, 6047 (1990).
4. Oxidation of 3-methoxy-10-hydroxy-9-anthrone (**5**) with potassium dichromate and  $H_2SO_4$  gave 2-methoxy-9,10-anthraquinone, identical with an authentic sample, mp.  $195^\circ$ , lit.<sup>8</sup>  $196^\circ$ .
5. D. Landini, *Synthesis*, 771 (1975).
- 6.a) R. F. Langler and T. T. Tidwell, *Tetrahedron Lett.*, 777 (1975); b) D. S. Bomse and T. H. Morton, *ibid.*, 781 (1975).
7. MMX force-field as implemented in the program MacroModel V 3.0.
8. M. M. Shemyakin, E. S. Chaman and A. A. Onishchenko, *Zhur. Obsch. Khim.*, **29**, 1831 (1959).
9. J. G. Topliss, L. M. Konzelman, N. Sperber and F. E. Roth, *J. Med. Chem.*, **7**, 453 (1964).

\*\*\*\*\*