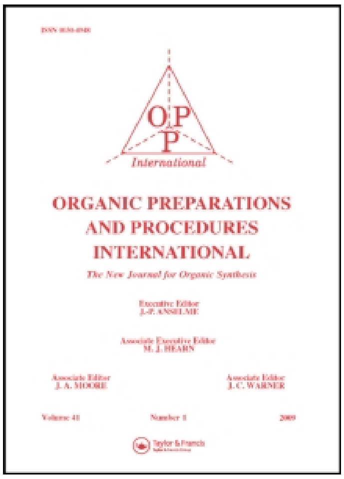

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1,1'-DIHYDROXY-2,2'-DIPHENYL-4,4'BINAPHTHYL

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1,1'-DIHYDROXY-2,2'-DIPHENYL-4,4'BINAPHTHYL

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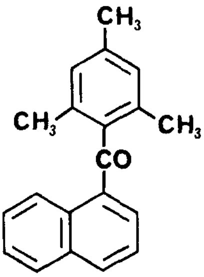
Identification of a product from the reaction between 1-mesitoylnapthalene I and phenylmagnesium bromide as 1,1'-dihydroxy-2,2'-diphenyl-4,4'-binaphthyl II (mp. 213.5-214.5°) corrects an earlier assignment[1] of the product as 2-phenyl-1-naphthol IV. The naphthol IV (mp 62.5-63°), 1,1'-(2,2'-diphenyl)-4,4'-binaphthone III, biphenyl, mesitoic acid and 1-mesitoyl-2-phenylnaphthalene are also produced by the reaction. Binaphthol II, binaphthone III and 2-phenyl-1,4-naphthoquinone-4-monoxime VI were otherwise obtained from 1-nitro-2-phenylnapthalene V by irradiation.[2]



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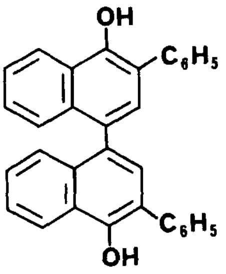

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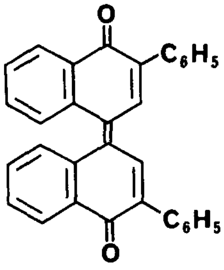

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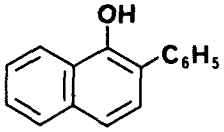

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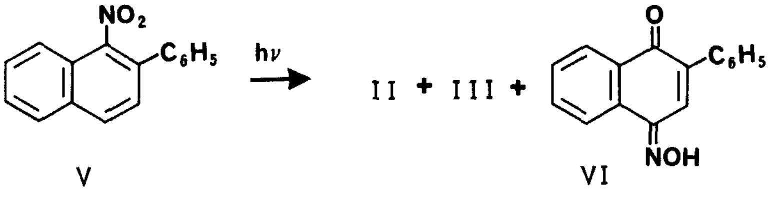

A reversible oxidation (by ferric chloride)-reduction (by sodium bisulfite) between the binaphthol II and the binaphthone III has been established. This supports earlier claims that the presumed naphthol IV, now identified as the binaphthol II was easily oxidized into a binaphthone.[3,4]

EXPERIMENTAL SECTION

Instruments included Perkin-Elmer 237B and 521 grating ir spectrophotometers, a Varian A-60 n.m.r. spectrometer, a Perkin-Elmer 270 mass spectrometer, and A.E.I. MS30 double-beam mass spectrometer and a Cary 14 spectrophotometer. Irradiations were carried out in a Rayonet RPR 100 photochemical chamber reactor (Southern New England Ultraviolet Co.) equipped with 16 low-pressure lamps having principal emission at 254 nm. Methanol was distilled from Linde molecular sieves Type 3A directly into the reactor tube. Each known product was identical with an authentic sample as shown by spectroscopic and/or mp comparison. Yields were based on starting material consumed. Chromatographic columns of silica gel were ca. 3 cm. diam. and 30-35 cm. long. Elemental analyses were provided by Micro-Tech Laboratories, Skokie, Illinois.

Photolysis of 1-Nitro-2-phenylnaphthalene V.- A solution of 1-nitro-2-phenylnaphthalene V (1.00 g, 0.004 mole) in anhydrous methanol (500 ml) was degassed under a stream of nitrogen for 12 hrs and irradiated at 254 nm for 72 hrs (the disappearance of the starting material was monitored by IR (1525 cm^{-1}) and tlc). The reaction mixture was concentrated and chromatographed on a silica gel column. n-Hexane (200 ml) eluted 0.19 g (19 %) of starting materials, followed by 1,1'-dihydroxy-(2,2'-diphenyl)-4,4'-binaphthyl II, as a colorless solid (0.38 g, 43%), mp. 213.5-214.5° (pet. ether). m/e(70 eV): M^+ 438; IR($CHCl_3$): 3510 cm^{-1} (-OH); nmr ($CDCl_3$): δ 5.7 (s, 2H, OH, exchangeable with D_2O); UV (EtOH), nm (log ε): 315 nm (4.6).

<u>Anal</u>. Calcd. for $C_{32}H_{22}O_2$: C, 87.65; H, 5.06
Found: C, 87.48; H, 5.23

A mixture (100 ml) of n-hexane-benzene (3:1) eluted 1,1'-(2,2'-diphenyl)-4,4'-binaphthone III as a dark purple solid (61 mg, 7.0 %), mp 235-240°.[1,3]

IR ($CHCl_3$): 1640 cm^{-1} (C=O); m/e (70 eV): M^+ 436.

Benzene (100 ml) eluted 2-phenyl-1,4-napthoquinone-4-monoxime VI as yellow needles (49 mg, 5 %), mp. 181-181.5°.

m/e (70 eV): M^+ 249; IR ($CHCl_3$): 3500 (C=N-OH), 1650 (C=O), 1640 (C=N-), 960 cm^{-1}; UV (n-hexane) nm (log ε): 345 (4.8), 301 (4.91); (EtOH), nm (log ε): 352 (4.86), 300 (4.96). The UV (methanol) absorption[5] for 1,4-naphthoquinone-4-oxime nm (log ε): 345 (3.9), 280 (4.2); (chloroform): 336 (3.9), 278 (4.2), (ether), 343 (3.9), 274 (4.3)); nmr: δ 7.1 (1H, s, olefinic proton of quinonoid ring).

<u>Anal</u>. Calcd. for $C_{16}H_{11}NO_2$: C, 77.10; H, 4.45; N, 5.62
Found: C, 76.82; H, 4.44; N, 5.50

A tar (44 mg) was obtained by elution with chloroform and methanol (tlc, several spots).

<u>Reaction of 1-Mesitoylnaphthalene I with Phenylmagnesium Bromide</u>.- A solution of 1-mesitoylnaphthalene I (5.0 g, 0.02 mole) in benzene (50 ml) was added to the Grignard reagent prepared from bromobenzene (21 g, 0.13 mole) and magnesium (3.2 g) in anhydrous ether (100 ml) at room temperature. Benzene (100 ml) was added to the reaction mixture and ether was allowed to evaporate until the temperature reached 55°. The colorless reaction mixture changed to orange after heating at

reflux for 75 hrs with constant stirring. The reaction mixture was cooled, treated with ice and dilute hydrochloric acid, washed with water and dilute sodium carbonate solution.[1] The dark residue obtained by removal of the solvent was dissolved in benzene (200 ml), treated with a stream of dry air for 7 days; extraction with dilute sodium bicarbonate solution (1 M, 100 ml) gave mesitoic acid (0.28 g, 8.3 %) upon acidification, mp 153-154°, tlc single spot. IR($CHCl_3$): 2950 (broad) and 1690 (-COOH) cm^{-1}; m/e (70 eV): M^+ 164.

The mother-liquor from the recrystallization of mesitoic acid gave 26 mg of colorless 2-phenyl-1-naphthol IV (0.6 %). The remaining organic layer was extracted by dilute sodium hydroxide (1 M, 100 ml). A dark oil obtained upon acidification in the concentrated hydrochloric acid was chromatographed on a silica gel column. n-Hexane (50 ml) eluted 2-phenyl-1-naphthol IV as colorless crystals (0.017 g, 3.7 %), mp 62.5°-63° (pet. ether), one tlc spot.

IR (CCl_4): 3570 cm^{-1} (-OH); m/e (70 eV): M^+ 220, 192, 191, 165, 115; nmr δ 5.9 (s, 1, OH) (exchangeable with D_2O).

Anal. Calcd. for $C_{16}H_{12}O$: C, 87.25; H, 5.49
Found: C, 86.98; H, 5.07

Further elution with n-hexane (100 ml) gave 1,1'-dihydroxy-(2,2'-diphenyl)-4,4'-binaphthyl II[1] as a colorless solid (0.11 g, 2.5 %), mp 211-212°, which became purple on standing in air.

IR (CCl_4): 3570 cm^{-1} (-OH); m/e (70 ev): M^+ 438; nmr ($CDCl_3$): δ 5.7 (s, 2 OH) (exchangeable with D_2O).

Organic layers insoluble in either sodium bicarbonate or sodium hydroxide were combined and chromatographed on a silica gel column. n-Hexane (100 ml) eluted colorless needles of biphenyl (1.99 g), mp. 53°; m/e (70 ev): M^+ 154.

Further elution with n-hexane (50 ml) gave 0.243 g of a dark yellow oil which did not solidify and showed several spots on a tlc plate. It gave a negative test with ferric chloride.[6] Further elution with n-hexane (50 ml) gave an orange oil which was recrystallized from petroleum ether to give 2-phenyl-1-naphthol IV (0.56 g, 12.5 %) as a yellow solid. The mixture (100 ml) of n-hexane and benzene (4:1) eluted 1-mesitoyl-2-phenyl-naphthalene[1] as colorless crystals (2.52 g, 35.4 %), mp 135-136° (tlc, one spot).

IR ($CHCl_3$): 1660 cm^{-1} (C=O); m/e (70 ev): M^+ 350.

Further elution with a mixture (50 ml) of n-hexane and benzene (4:1) gave 1,1'-dihydroxy-2,2'-diphenyl-4,4'-binaphthyl II (0.74 g, 16.6 %). A dark purple solid (0.55 g, 12.4 %) of 1,1'-(2,2'-diphenyl)-4,4'-binaphthone III was eluted by a mixture (50 ml) of hexane-benzene (1:1), mp 235-240°. Elution by a mixture (100 ml) of n-hexane and benzene (1:2) gave an unidentified orange yellow oil (0.05 g). Benzene, chloroform and methanol eluted a tar (2.2 g) which showed several spots on the tlc plate.

Ferric Chloride Oxidation of 1,1'-Dihydroxy-2,2'-diphenyl-4,4'-binaphthyl II.- To a solution of 1,1'-dihydroxy-2,2'-diphenyl-4,4'-binaphthyl II in methanol, a solution of ferric chloride in methanol was added dropwise until the reaction mixture became dark purple.[6] The reaction mixture was treated with water, extracted with methylene chloride and the extract was dried ($MgSO_4$). Evaporation left a quantitative yield of 1,1'-(2,2'-diphenyl)-4,4'- binaphthone III as a purple crystalline solid.

Sodium Bisulfite Reduction of 1,1'-(2,2'-Diphenyl)-4,4'-binaphthone III.- An aqueous solution of sodium bisulfite was added dropwise to a warm suspension of 1,1'-(2,2'-diphenyl)-4,4'-binaphthone III in methanol until the dark purple color disappeared.[7] The mixture was heated on the steambath for 5 min., treated with cold water, and extracted with methylene chloride. The extract was dried and evaporated to give a quantitative yield of 1,1'-dihydroxy-2,2'-diphenyl-4,4'-binaphthyl II as a colorless solid, mp 210-211°.

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