

Dianionic oxy-cope rearrangement of 9,10-dihydroxy-9,10-di-1¹-naphthyl phenanthrene

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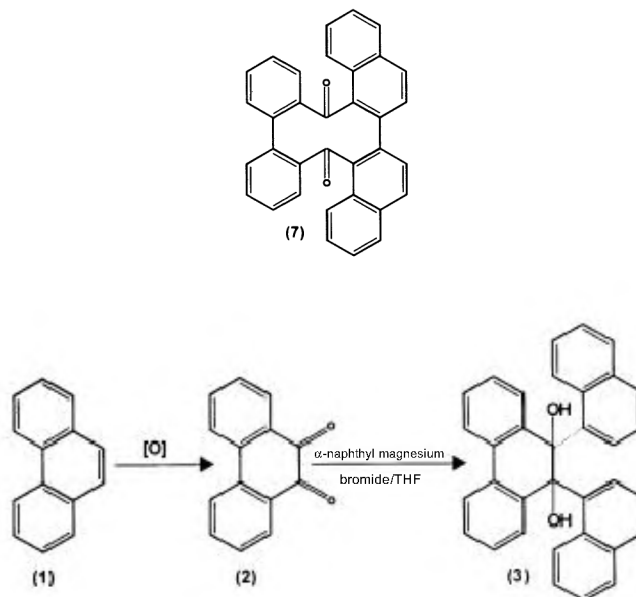
We report here the dianionic oxy-cope rearrangement of dinaphthyl diol (3) where the pi bonds of the two naphthalene rings form the 1,5-hexadiene system necessary for the [3,3] sigmatropic shift.

ANIONIC oxy-cope rearrangements of divinyl carbinols have been well documented¹. The dianionic oxy-cope rearrangement of 1,2-divinyl-1,2-diols was first reported in 1982 (ref. 2); other dianionic oxy-cope rearrangements have been reported thereafter³. But there is no report on the dianionic oxy-cope rearrangement of 9,10-dihydroxy-9,10-di-1¹-naphthyl phenanthrene. The present work deals with the synthesis and rearrangement of 9,10-dihydroxy-9,10-di-1¹-naphthyl phenanthrene, where the divinyl moiety is a part of the naphthalene rings.

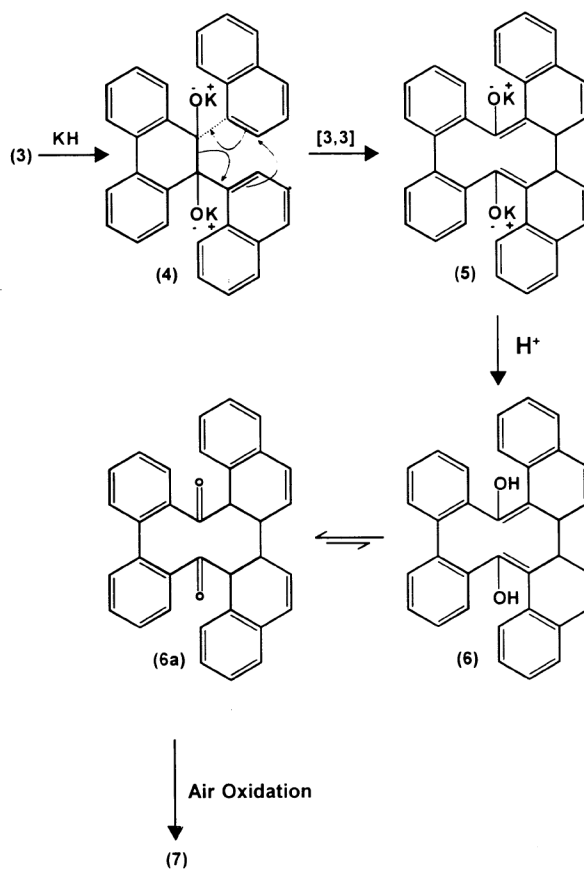
The synthesis of 9,10-dihydroxy-9,10-di-1¹-naphthyl phenanthrene from phenanthrene was carried out as in Scheme 1.

Phenanthrene (1) on oxidation with chromium trioxide in concentrated sulphuric acid gave phenanthrene-9,10-dione (2) (ref. 4). Treatment of phenanthrene-9,10-dione (2) with four equivalents of α -naphthyl magnesium bromide in THF at reflux temperature for 2 h gave 9,10-dihydroxy-9,10-di-1¹-naphthyl phenanthrene (3), melting point 210–212°C. The IR spectrum showed the absence of carbonyl group and the presence of tertiary-OH around 3505 cm⁻¹. PMR (CDCl₃) showed δ 1.60, 2.20 (2s, 2H, -OH), 7.40 (m, 20H) aromatic protons and 8.20 (m, 2H) periprotons of naphthalene. Mass spectrum showed M⁺ ion at m/z = 464. Based on analogy^{5,6}, the dinaphthyl diol has been assigned the *trans* configuration in which the dinaphthyl moieties must be dipseudo equatorial.

Treatment of diol (3) with two equivalents of potassium hydride in THF at reflux temperature for 2 h gave a white crystalline solid; mp = 162–164°C, yield 69%. The IR spectrum showed the absence of -OH absorption and presence of 3050 (C-H, str), 1660–1670 (>C=O, aryl carbonyl) and 1600 cm⁻¹ (>C=C, str, aryl). PMR (CDCl₃/TMS) showed δ 7.5 (m, 18H) aromatic protons, δ 8.50 (m, 2H) periprotons of naphthalene and mass spectrum M⁺ ion at m/z = 460. These spectral data and elemental analysis are in agreement with the structure (7) given below.



Scheme 1.



Scheme 2.

The transformation of (3) to (7) can be rationalized as shown in scheme 2.

A [3,3] sigmatropic shift in (4) will give (5). Neutralization followed by tautomerization will give (6a)

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which on air oxidation gives (7). Direct air oxidation of the dienolate (5) to the dione (7) is also possible under the reaction conditions before neutralization. A similar air oxidation of dihydro-azulene to azulene has been reported⁷.

The rearrangement product (7) shows two low-field protons at δ 8.5 when compared with the diol (3). This difference can be accounted for since structure (7) has two periprotons of the naphthalene rings proximate to two carbonyl groups⁸.

All melting points are uncorrected. IR spectra were recorded on a Shimadzu 8201 instrument. PMR spectra were recorded on Bruker DPX-200, 200 MHz FT NMR instrument employing tetramethyl silane as internal standard. Mass spectra were recorded on Varian Mat CH-7 Mass Spectrometer and also Shimadzu Q.P.5000 mass spectrometer.

Phenanthrene-9,10-dione⁴ (2) was prepared by the oxidation of phenanthrene with chromium trioxide in conc. H₂SO₄.

For the preparation of 9,10-dihydroxy-9,10-di-1¹-naphthyl phenanthrene (3). To a solution of α -naphthyl magnesium bromide prepared from magnesium (1.92 g, 0.08 g atom) and α -bromonaphthalene (16.6 g, 0.08 m) in dry THF (100 ml) was added a slurry of phenanthrene-9,10-dione (4.16 g, 0.02 m). After refluxing for 2 h, saturated ammonium chloride solution (50 ml) was added with stirring. Then the organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was dried. On removal of the solvent, a viscous oil (5.91 g) was obtained.

This viscous oil was chromatographed over a column of silica gel. Elution with ethyl acetate : petrol (1 : 4) gave a white solid, melting point 210–212°C. Yield based on reacted dione (2) was 3.2 g (61%). Further elution with ethyl acetate : petrol (1 : 3) gave unreacted phenanthrene-9,10-dione (1.8 g).

Let us consider the rearrangement of 9,10-dihydroxy-9,10-di-1¹-naphthyl phenanthrene (4). To a suspension of potassium hydride (0.2 g, 0.005 m, 0.53 g of a 30% dispersion in mineral oil washed with 10 ml portions of dry petrol) in dry THF (40 ml) was added a solution of diol (3) (0.29 g, 0.0001 m) in THF (25 ml). The mixture was refluxed in an atmosphere of nitrogen for 2 h. The solvent was removed and saturated ammonium chloride (10 ml) was added to the residue. The aqueous solution was extracted with chloroform (3 \times 5 ml). The chloroform extract was washed with water (150 ml), brine (100 ml) and dried. Removal of the solvent under reduced pressure gave a white crystalline solid, melting point 164°C (ethylacetate : petrol), yield 0.2 g (69%).

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RAPD markers reveal narrowing genetic base of Indian tomato cultivars

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Genetic diversity of 27 tomato cultivars grown in India was analysed with RAPD markers, generated by 42 random primers. The overall high levels of pair-wise similarity (Jaccard's mean = 0.825) and low levels of marker diversity (mean = 0.165) implied the existence of limited genetic variation in the investigated materials. Interestingly, old introductions and locally developed cultivars of the 1970s exhibited significantly greater genetic variation than the ones released during the 1990s. Reduction in the genetic diversity among modern tomato cultivars may be attributed to the recent trend towards breeding for similar plant and fruit characteristics.

TOMATO (*Lycopersicon esculentum* Mill.) is one of the most important vegetable crops grown in India. With an annual production of 5.4 million Mt, the country is the sixth largest tomato producer in the world¹. Though concrete historical records of its first introduction into the country from its primary centre of diversity in South America do not exist, tomato is presumed to have been brought here during the second half of the 16th century through Far Eastern countries². Nineteenth century plant

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