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SYNTHESIS OF A NEW HYDROCARBON 6,12-DIHYDROANTHANTHRENE

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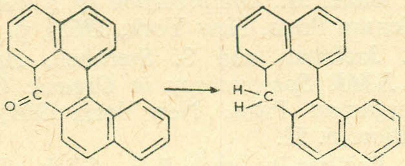
Abstract. A new polycyclic hydrocarbon 6,12-dihydroanthanthrene has been synthesised from 8,8′-bisbromomethyl-1, 1′-binaphthyl by its reduction with phenyllithium. Characteristic properties of its IR, UV, PMR and mass spectra have been studied.

Polycyclic hydrocarbons are of great interest in several areas of theoretical, physical, organic and biological chemistry. The methods for their prepartion generally consist in the reduction of a quinone or an oxygen containing compound. Naphtho-1′,2′,7,8-perinaphthalene (II) is obtained by the reduction of perinaphthenone (I) with aluminium isopropylate.[1] Attempts to reduce anthanthrone (III) to give 6,12-dihydroanthanthrene (IV) were unsuccessful. Clemensen reduction, however, produces the hydrocarbon in very small quantity which could not be isolated and purified by normal techniques as also by the layer chromatography technique. The hydrocarbon is, therefore, separated and purified by the radiodilution technique.



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Consequent upon these experimental evidences, a new route for the synthesis of 6,12-dihydroanthanthrene has been evolved which utilises 8,8′bisbromomethyl-1,1′-binaphthyl, the synthesis of which has been reported earlier[2] as the starting material. The reduction of dimethyl-1,1′-binaphthyl-8, 8′-dicarboxylate (V) with lithium aluminium hydride yields 8, 8′-bishydroxymethyl-1, 1′-binaphthyl (VI) which is converted into its dibromide (VII) by treating with hot hydrobromic acid. The dibromide gives the new hydrocarbon 6,12-dihydroanthanthrene on treatment with phenyllithium. Schematic representation of the sequence of the reactions is shown in Chart 1.

6,12-Dihydroanthanthrene crystallises from petroleum ether in white shiny crystals, m.p. 150–151°C which forms picrate, m.p. 115–116°C. It does not dissolve in cold sulphuric acid but produces an orange red flourescence. The solution in organic solvents is colourless with a blue flourescence.

nm	ε	$\log_{10}\varepsilon$
310.0	(9160)	3.9619
296.0	(11690)	4.0678
229.0	(29670)	4.4723
212.0	(26730)	4.4270

The IR spectrum of the hydrocarbon showed strong stretching vibrations of $>CH_2$ groups at 2940 cm^{-1} and the benzenoid stretchings showed small bands at 1600 and 1585 cm^{-1}. The three most intense bands in the spectrum appeared at 826, 780 and 774 cm^{-1} and the rest of the supporting bands at 1460, 1445, 1342, 1312, 1205, 1042, 1029, 970, 913, 881 and 861 cm^{-1}.

The PMR spectrum of the hydrocarbon in carbon tetrachloride showed a singlet at τ 6.85 for two methylene groups at positions 6 and 12. This sharp singlet is due to the identical environment in the molecule. The benzenoid protons H_2, H_3, H_8 and H_9 appeared as a multiplet at τ 1.79. The protons H_1, H_5, H_7 and H_{11} appeared at τ 2.21 and the protons H_4 and H_{10} as a double doublet at 2.65 thus accounting for all the 14 protons in the molecule.

The mass spectrum of 6,12-dihydroanthanthrene showed a molecular ion peak at m/e 278^+ according to the formula $C_{22}H_{14}$. This is the most abudant ion peak in the whole spectrum.

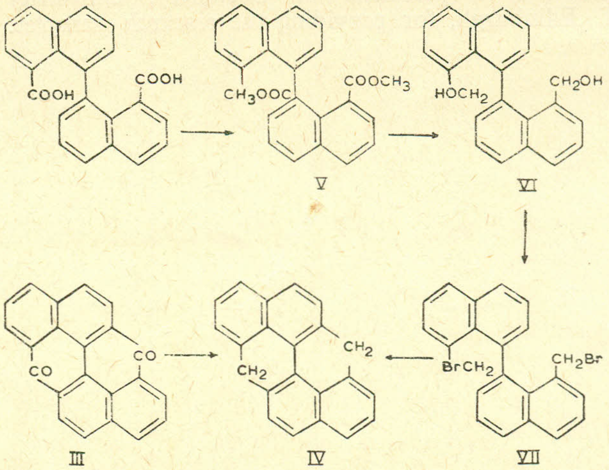

Chart. 1.

It showed a moderate peak $(M-1)^{+}$ at m/e 277^{+} (20% of M^{+}) corresponding to the loss of 1 hydrogen atom. The $(M-2)^{+}$ appeared at m/e 276^{+} (25% of M^{+}) corresponding to the loss of 2 hydrogen atoms. The $(M-2)^{+}$ ions are formed alongwith an extensive ring opening.[3]

In the case of spectra of other aromatic hydrocarbons such as naphthalene, azulene[4] and phenanthrene 6,12-dihydroanthanthrene also exhibited a mass spectral peak $(M-C_2H_2)^{+}$ at m/e 252^{+} (16.6% of M^{+}) representing the loss of acetylene during decomposition. The loss of acetylene necessitates ring opening although subsequent ring closure is not precluded.[3] There is also a very significant peak at m/e 239^{+} (7.6% of M^{+}) corresponding to the loss of 39 mass units (C_3H_3). The $(M-C_4H_4)^{+}$ peak at m/e 226^{+} (1.8% of M^{+}) represents the loss of two acetylene molecules which can occur only with a very profound disruption of the molecule. The peaks at m/e 264^{+} (15.7% of M^{+}) and m/e 250^{+}(6.6% of M^{+}) represent the loss of 14 mass units (CH_2) and 28 mass units (C_2H_2) respectively.

In addition to the main fragment ions which correspond to the loss of one or two hydrogen atoms or to the loss of C_2H_2, C_3H_3, and C_4H_4 groups from the parent ion, it exhibited a number of doubly charged ions which is a general feature in mass spectra of aromatic hydrocarbons. The doubly charged parent ion M^{2+} appeared at m/e 139^{+} (15.7% of M^{+}) and a doubly charged isotopic ion M^{2+} at m/e $139\frac{1}{2}^{+}$. Ions at m/e $138\frac{1}{2}$ (2.5% of M^{+}) and $137\frac{1}{2}^{+}$ (1.25% of M^{+}) correspond to $(M–H)^{2+}$ and $(M–3H)^{2+}$ and the ion at m/e 138^{+} to $(M–2H)^{2+}$.

MASS SPECTRAL DATA OF 6,12-DIHYDROANTHANTHRENE.

Process	m/e of ion	Relative abundance
$C_{22}H_{14}\xrightarrow{-e}C_{22}H_{14}^{+}$	278	100
$\xrightarrow{-H}C_{22}H_{13}^{+}$	277	20
$\xrightarrow{-2H}C_{22}H_{12}^{+}$	276	20
$\xrightarrow{-C_2H_2}C_{20}H_{12}^{+}$	252	16.6
$\xrightarrow{-H_2C_3}C_{20}H_{11}^{+}$	251	2
$\xrightarrow{-C_3H_3}C_{19}H_{11}^{+}$	239	7.6
$\xrightarrow{-2C_2H_2}C_{18}H_{10}^{+}$	226	1.8
$\xrightarrow{-CH_2}C_{21}H_{12}^{+}$	264	14.7
$\xrightarrow{-2CH_2}C_{20}H_{10}^{+}$	250	6.6
$\longrightarrow C_{22}H_{14}^{2+}$	139	15.7
$\longrightarrow C_{23}H_{13}^{2+}$	$138\frac{1}{2}$	2.5
$\longrightarrow C_{22}H_{12}^{2+}$	138	5.5
$\longrightarrow C_{20}H_{12}^{2+}$	126	7

The ions described above are due both to the singly and doubly charged ions; the $139\frac{1}{2}$ peak being only the isotopic M^{2+}. A number of doubly charged ions of less importance is also to be mentioned in the region between 100–140.

A triply charged molecular ion M^{3+} at m/e $92\frac{2}{3}^{+}$ and $(M-1)^{3+}$ at m/e $92\frac{1}{3}^{+}$ both of very low intensity also appear in the spectrum.

Experimental

Dimethyl-1,1′-binaphthyl-8,8′-dicarboxylate. Powdered 1,1′-binaphthyl-8,8′-dicarboxylic acid (5.0 g) was added to the cold ethereal solution of diazomethane (70 ml, 1.2 g). The reaction proceeded with effervescence yielding a white solid mass precipitated at the bottom of the reaction flask. The solid mass was filtered washed well with $NaHCO_3$ solution followed by washings with water and dried (4.5 g), m.p. 156–158°C. Recrystallisation from methylated spirit yielded thick needles, m.p. 158–159°C.

8,8′-Bishydroxymethyl-1,1′-binaphthyl. Lithium aluminium hydride (1.5 g, 6 mole) was placed and quickly covered with absolute ether (500 ml) in a three-necked flask fitted with a condenser and a dropping funnel. A suspension of dimethyl-1, 1′-binaphthyl-8, 8′-dicarboxylate (5.0 g; 1 mole) in 1 litre absolute ether was gradually added to the mixture and heated on a water-bath for ca. 3–4 hr. The excess metal hydride was decomposed by water and sulphuric acid (2N). The organic layer was separated and the aqueous layer further extracted with ether using 100 ml each time. The ethereal layers were combined together and dried ($CaCl_2$) overnight. The solvent was distilled in vacuum when a crystalline substance was obtained, m.p. 145–150°C. It was recrystallised from benzene, m.p. 151–152°C.

8,8′-Bisbromomethyl-1,1′-binaphthyl. To a solution of 8,8′-bisyhdroxymethyl-1, 1′-binaphthyl (5.0 g) in hot glacial acetic acid (125 ml) was slowly added hot HBr (60 ml; $d = 1.5$). The mixture was stirred and allowed to stand for some time. A light yellow crystalline mass separated. HBr (25 ml.) was further added to the mixture. On cooling, the solid mass was filtered off, washed with water and dried, 8.0 g, m.p. 178-190°C. Crystallisation from chloroform gave very light yellow crystals, m.p. 190–191°C.

6,12-Dihydroanthanthrene. Phenyllithium was prepared by the addition of 4 ml bromobenzene in 25 ml absolute ether to a well-stirred suspension of 0.5 g lithium wire in 250 ml dry ether. It was refluxed for 3–4 hr with constant stirring under N_2 atmosphere. A solution of 8,8′-bisbromomethyl-1, 1′-binaphthyl (2.0 g) in dry benzene was added to the phenyllithium drop by drop in 30 min. It was further refluxed under N_2 atmosphere for 4 hr. The resultant product was decomposed with water and dilute H_2SO_4. The organic layer was separated and the aqueous layer was further extracted three times with 100 ml ether each time. The ethereal layers were combined together, washed with water and dried (Na_2SO_4). The solvent was removed and the residue extracted with petroleum ether which on concentration gave white shining crystals, m.p. 150–151°C. (Found: C, 94.7; H, 5.3%. Calc. for $C_{22}H_{14}$: C, 94.9; H, 5.1%.)

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