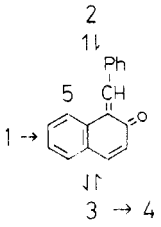
Scheme II



in the base-catalyzed condensation of hydroxybenzyl alcohol.[8] If such a product as **5** is present, the pathway could be depicted as in Scheme II. We are now making our effort to trap **5** or to seek unambiguous evidence supporting the intervention of **5**.

Experimental Section

Proton and ^{13}C NMR spectra were recorded on a JEOL JNM-FX-60 (Me_4Si as internal standard) spectrometer and IR spectra on a Shimadzu IR-408 spectrometer. MS spectra were obtained on a JEOL JMS-DX300 (70 eV) spectrometer. Gas and liquid chromatographies were performed with Yanagimoto G-180 and Toyo Soda HLC-802UR spectrometers, respectively. Melting points were determined and uncorrected on a Meihoh MP-2 spectrometer.

Alkylation of 2-NK with Benzyl Alcohol at 180 °C (Effect of Added Benzaldehyde). In a flask equipped with a thermometer, a mechanical stirrer, and a reflux condenser whose top was connected to a 100-mL Erlenmeyer flask containing liquid paraffin were placed 2-NK (5.49 g, 0.0302 mol) and phenyl ether (30.2 g). The mixture was stirred at 180 °C for 2 h in a stream of oxygen-free nitrogen through a column packed with oxygen absorber (OXISORB L). In this mixture benzyl alcohol (5.23 g, 0.0484 mol) was added through a dropping funnel, and the whole mixture was kept at this temperature for additional 3 h, but no reaction occurred (this was confirmed by gas chromatography). Then, the addition of benzaldehyde (0.99 g, 0.0093 mol) caused the formation of **4** (0.0179 mol/4 h) and the consumption of benzyl alcohol (0.0115 mol/4 h).

Temperature Dependence of the Formation of 1, 2, 3, and 4. A mixture of 2-NK (1.48 g, 8.13 mmol), benzyl alcohol (70 g), and phenyl ether (0.96 g, as an internal standard) was heated at a rate of 0.5 °C/min in a nitrogen stream. At 68 °C, benzaldehyde (1.00 g, 9.43 mmol) was added, and occasional sampling was made to determine the amounts of **1**, **2**, **3**, and **4** by liquid chromatography. The results are shown in Figure 1.

Preparation of 1-(α-Hydroxybenzyl)-2-naphthol (1). A mixture of 2-NK (30.2 g, 0.166 mol) and benzaldehyde (53.8 g, 0.508 mol) was stirred for 5 h at room temperature. Precipitates were collected, washed with aqueous HCl and water, and recrystallized from benzene to give **1**, 24.0 g, (58%): mp 114 °C; MS (70 eV), *m/e* (relative intensity) 250 (M^+, 14), 231 (base peak, 100), 202 (12), 78 (11); ^1H NMR (δ value, in acetone-d_6) 6.34 (s, 1 H, C-OH), 6.86–7.98 (m, 12 H, Ar H + methyne proton), 9.88 (s, 1 H, Ar OH) [signals at 6.34 and 9.88 disappeared by addition of D_2O]; ^{13}C NMR (ppm, in acetone-d_6) 72.6 (methyne carbon, off-resonance method; 70.7 and 74.1), 119.7–129.7 (aromatic carbons); IR (cm^{-1}) 3400 (s), 830, 815 (m), 755 (s, with a shoulder), 710 (s, with a shoulder).

Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.77; H, 5.71.

Preparation of Benzylidene-1,1′-bis(2-naphthol) (2). A mixture of 2-NK (20.3 g, 0.112 mol) and benzaldehyde (35.9 g, 0.339 mol) was stirred at 100 °C for 9 h. After usual workup, precipitates were recrystallized from ether/cyclohexane (1:2) to afford **2**, 11.3 g (54%): mp 187 °C; MS, (*m/e*) 376 (M^+, 9), 234 (13), 233 (38), 232 (50), 231 (base peak, 100), 202 (15), 144 (30), 115 (12), 44 (29); ^1H NMR (in Me_2SO-d_6) 7.07–8.22 (m, 18 H, Ar H + methyne proton), 9.70 (s, 2 H, OH); ^{13}C NMR (in Me_2SO-d_6) 41.5 (methyne carbon; off-resonance method; 40.1 and 42.8), 117.1–152.7 (aromatic carbons); IR (cm^{-1}) 3200 (br, OH), 810 (s, with a shoulder), 743 (s, with two shoulders), 705 (m).

Anal. Calcd for $C_{27}H_{20}O_2$: C, 86.14; H, 5.36. Found: C, 85.94; H, 5.39.

Alternative Synthesis of 2. Heating a mixture of **1** (2.00 g, 0.0080 mol) and 2-naphthol (10.0 g, 0.0694 mol) at 130 °C for 3 h gave **2**, 2.64 g (88%).

Preparation of 1-[α-(Benzyloxy)benzyl]-2-naphthol (3). A mixture of **1** (2.00 g, 0.0080 mol) and benzyl alcohol (10.0 g, 0.0926 mol) was heated at 115 °C for 3 h. After usual workup, **3** was obtained in a yield of 2.02 g (74%): mp 119 °C; MS, (*m/e*) 340 (M^+, 26), 234 (54), 233.1 (41), 233.0 (42), 232 (base peak, 100), 231 (85), 203 (65), 202 (67), 116 (44), 108 (49), 107 (53), 101 (52); ^1H NMR (in acetone-d_6) 4.62 (s, 2 H, methylene H), 6.69–8.16 (m, 17 H, Ar H + methyne H), 9.19 (s, 1 H, OH); ^{13}C NMR (in acetone-d_6) 71.3 (methylene carbon, off-resonance method; 68.0, 71.0, and 73.9), 77.7 (methyne carbon, off-resonance method; 75.7 and 79.0), 116.1–153.7 (aromatic carbons).

Anal. Calcd for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92. Found: C, 84.46; H, 6.01.

Conversion of Precursors under Various Conditions. A representative example (ex. no. 4 in Table I) is described. A mixture of **2** (0.31 g, 0.82 mmol), potassium benzyl oxide (1.64 mmol, as a solution (2.05 g) of benzyl alcohol), benzyl alcohol (50.0 g), and phenyl ether (0.16 g, as an internal standard) was placed in a flask. After displacement of the atmosphere with nitrogen, the mixture was heated at 120 °C for 150 min and then at 170 °C for 60 min. During the reaction, occasional samplings were made for the reaction mixture by means of a syringe. Quantitative analyses of **1**, **2**, **3**, **4**, and 2-naphthol were performed by liquid chromatography. The results are listed in Table I.

Registry No. **1**, 40473-53-8; **2**, 29114-24-7; **3**, 98577-46-9; **4**, 36441-31-3; 2-NK, 36294-21-0; benzyl alcohol, 100-51-6; benzaldehyde, 100-52-7; 2-naphthol, 135-19-3; potassium benzyl oxide, 22379-62-0.

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The Stereoisomers of Perhydrophenanthrene

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There are six stereoisomers possible for perhydrophenanthrene (excluding enantiomers), four of which have been described in the literature.[1] Because this series contains one isomer with the central cyclohexane ring in a boat conformation and another with a syn-diaxial interaction, and because of the widespread occurrence of the perhydrophenanthrene skeleton in nature, the relative stabilities of the possible stereoisomers are of interest. The conformational analysis of these compounds was carried out at an early date,[1-9] and the pertinent conformations are shown in Figure 1.

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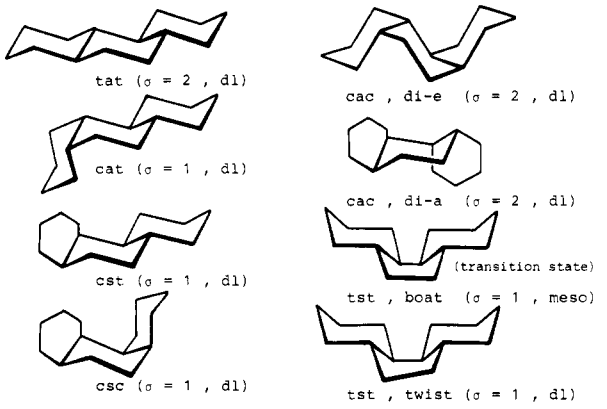

Figure 1. Stereoisomers of perhydrophenanthrene.

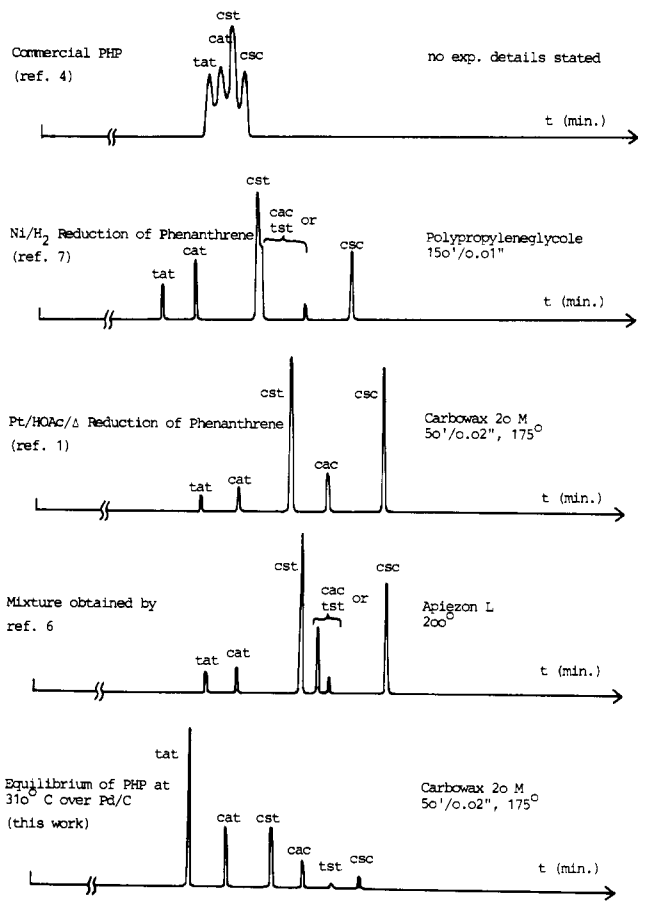

Figure 2. Chromatograms of various perhydrophenanthrene mixtures.

From a classical point of view, perhydrophenanthrene has two meso stereoisomers, and four which are *dl* pairs. But the meso ones are not meso in a thermodynamic sense. The tst isomer consists of a *dl* pair, separated by a small energy barrier. So for thermodynamic purposes, it is a *dl* pair, even though because of the small barrier it is not a resolvable compound. For the csc isomer, the barrier must be much more substantial, since to surmount it involves chair to boat transformations of cyclohexane rings, plus a number of apparently severe steric interactions. Again, as far as the thermodynamics, this is not relevant. The compound is instantaneously a mixture of a pair of enantiomers.

There have been several attempts to estimate or calculate the relative stabilities of these isomers.[1-7] Also, some analyses of equilibrated mixtures or otherwise obtained samples of perhydrophenanthrene by gas-phase chromatography have been previously reported[1,6,7,8] (Figure 2). The cac and tst isomers had not been prepared with known stereochemistries and could not be assigned in the earlier chromatograms. Thus it was deemed desirable to carry out a more careful equilibration study in this series. By determining the composition of the equilibrated mixture as a function of temperature, it was thought that it would be possible to obtain the enthalpies and entropies for each of the isomerization equilibria under consideration. The MM2 force field has now become available and should also permit independent determination of the relative energies of these stereoisomers, with greater reliability than was possible earlier.

Table I. Enthalpies and Entropies of Isomerization by Direct Measurement

isomer	ΔH, kcal/mol	ΔS, eu
cat	7.13	8.49
cst	11.59	16.25
cac	8.67	6.85
csc	22.04	24.47
tst	22.87	23.74

Table II. Theoretical Entropies (eu) of Symmetry and Mixing for the Perhydrophenanthrenes

isomer	symmetry no.	ΔS_{symm}[a]	ΔS_{mix}[a]	ΔS_{total}[c]
tat	2(*dl*)	−1.38	1.38	0.00
cat	1(*dl*)		1.38	1.38
cst	1(*dl*)		1.38	1.38
cac, di-e	2(*dl*)	−1.38		
			1.90[b]	0.52
cac, di-a	2(*dl*)	−1.38		
tst, twist	1(*dl*)			
			1.38[b]	1.38
tst, boat	1(meso)			
csc	1(*dl*)		1.38	1.38

[a] According to ref 10. [b] Contains also ΔS_{mix} for higher energy conformers. ΔH(cac(di-a) − cac(di-e) = 1.40 kcal/mol. ΔH(tst-(boat) − tst(twist)) = 0.55 kcal/mol. For the tst, the boat is a transition state separating a degenerate pair of the twists. Since the barrier height is less than 7 kcal/mol, ΔH is increased by 0.36 kcal/mol from the torsional effect in the MM2 calculation.[16] The entropy should also be increased. In the absence of a way to estimate this latter increase, we have used the 1.38 eu value, as if the barrier were higher than room temperature. [c] $\Delta S_{total} = \Delta S_{rel}$.

Results and Discussion

The assignments of the various structures to the peaks follow those given in ref 1, except that here it proved possible to locate the isomer missing from the earlier work, and it seems clear enough which is the cac and which is the tst isomer from the relative heights of the peaks on the chromatogram obtained here, together with the MM2 energy calculations.

It is reasonably easy to determine the values for the free energy differences of the various isomers from data of the kind shown by the last chromatogram in Figure 2. An attempt was made to break these free energies down into enthalpies and entropies by means of a plot of ln K against $1/T$. The values found for ΔH and ΔS are given in Table I, but these are considered to be completely unreliable. The temperature range used was not very great, and the changes in the relative peak areas were difficult to measure accurately because off the wide variation in the peak sizes. Since these numbers are clearly meaningless, while the measured values for ΔG are believed to be reasonably good, the theoretical entropies of symmetry and mixing for the individual isomers (Table II) were used to calculate the enthalpies from the ΔG values obtained experimentally.

The ΔG values at the highest temperature (348 °C, to ensure that equilibrium was reached) were used, together

Table III. Relative Enthalpies for the Perhydrophenanthrenes from Equilibrium Studies and Calculations (kcal/mol)

isomer	Johnson,[2] 1953, est	Dauben,[3] 1956, est	Grant,[4] 1974, est	Sandorfy,[5] 1966, est	Aref'ev,[6] 1972, est	MM,[1] 1971	MM1,[17] 1973	MM2, 1979	this work, exptl
tat	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
cat	2.4	2.4	2.7	2.67	2.7	2.57	2.34	2.63	2.66 ± 0.22
cst	2.4	2.4	2.7	2.66	2.7	2.44	2.10	2.53	2.25 ± 0.18
cac di-e							5.09	5.54	
	4.0	4.0	4.5	4.47	5.4	4.01	3.70	4.27	4.60 ± 0.36
di-a							3.59	4.14	
tst twist							7.17	7.49	
	4.8	6.4	4.5	9.74	5.6	7.03	7.32	7.85	8.98 ± 0.70
boat							8.28	8.04	
csc	6.4	7.2-8.2	9.2	7.29	7.5	9.01	8.22	8.46	7.43 ± 0.56

Table IV. Perhydrophenanthrene Isomer Percentage Compositions at Equilibrium[a]

isomer	temp, °C (time, h) 278 (600)	305 (158)	323 (68)	348 (46)
tat	82.1	77.0	72.8	62.9
cat	9.0	10.9	12.2	14.5
dcst	7.9	10.8	13.5	20.3
cac	1.0	1.2	1.4	1.9
tst	0.01	0.03	0.05	0.08
csc	0.04	0.07	0.1	0.3

[a] Gc conditions: Perkin-Elmer F11 chromatograph, support coated capillary column, Carbowax 20 M, 50 ft × 0.02 in. (Perkin-Elmer); carrier gas, N_2; detector, FID. The retention times of the perhydrophenanthrenes were all found to be in the range of 3–5 min, whereas the side products needed over 10 min to elute.

with the values for ΔS_{rel} in Table II, to calculate the values for ΔH. These values, together with estimated and calculated values which appeared in the earlier literature are summarized in Table III. The errors listed correspond to twice the average deviations in the experimental values. The agreement is good except for the two least stable isomers, where the discrepancy between experimental and the MM2 values is about 1 kcal/mol in each case.

The tst compound should have its energy calculated rather accurately. The conformational enthalpy of the twist form of cyclohexane has been directly measured[11] and indirectly measured in substituted compounds,[12,13,14] to yield values of 5.5, 5.9 ± 0.6, 5.5 ± 0.4, and 4.8 ± 0.9, respectively. These values are all in good agreement with each other, and the MM2 value of 5.36 kcal/mol is also in agreement with them. The X-ray structure of a derivative of this ring system has been reported recently,[15] and the geometry found for ring B is almost exactly as calculated by MM2. The reliability of the calculated energy for the csc isomer is hard to assess, since no good value for an analogue is experimentally known. We would take the "best value" for the energy of this compound to be the average of the experimental and MM2 values (7.95 kcal/mol).

Experimental Section

Perhydrophenanthrene (a mixture containing 0.4% tat, 3.2% cat, 38.6% cst, 7.2% cac, and 50.6% csc) was obtained by hydrogenation of phenanthrene in acetic acid with the aid of reduced platinum oxide catalyst. The reaction was carried out at 40–60 psi of pressure at 70 °C, one replacement of the catalyst being necessary to bring the reaction to completion. Equilibration was then carried out on the neat material at 270–350 °C in sealed glass tubes in the presence of 10% Pd/C catalyst. The equilibrated liquid was filtered, diluted with pentane, and analyzed by gas chromatography. The individual isomers were identified by comparison with already known physical constants and behavior on GC or by their relative peak areas before and after equilibration.[9] The assumption was made that equilibrium was reached in each case, which was shown to be correct earlier with the perhydroanthracenes.[9] Some side products, probably from dehydrogenation, were noted, but none of them interfered with the analysis. These higher boiling side products seemed to increase in amount approximately in proportion to the less stable perhydrophenanthrene isomers at higher temperatures, and thus they are very likely at equilibrium too.

The percentage of each isomer in the equilibrium mixture at each temperature was recorded as an average of at least five determinations. The product ratios of the less stable isomers were always checked against the next higher peak in attenuated chromatograms. The numbers are summarized in Table IV.

Acknowledgment. We are grateful to the National Science Foundation (Grant CH 8315543) for support of this work.

Registry No. Pd, 7440-05-3; *tat*-perhydrophenanthrene, 2108-89-6; *cat*-perhydrophenanthrene, 27389-73-7; *cst*-perhydrophenanthrene, 27425-35-0; *cac*-perhydrophenanthrene, 27389-74-8; *tst*-perhydrophenanthrene, 27389-76-0; *csc*-perhydrophenanthrene, 26634-41-3; phenanthrene, 85-01-8.

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Baeyer–Villiger Oxidation of Naphthaldehydes: Easy Access to Naphthoquinones

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Recently, we[1,2] reported that various 1-naphthaldehydes could be easily obtained by the cycloaddition of an isoquinolinium salt with vinyl ethers. The method was an extension of that first developed by Bradsher[3] and later modified by Falck.[4] We were primarily interested in using this reaction for the synthesis of quinone antibiotics via the naphthaldehydes.

Two possible routes were considered to determine the feasibility of converting 1-naphthaldehydes to 1,4-naphthoquinones. One scheme was the conversion of 1-

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