

REGIOSPECIFIC CATALYTIC HYDROGENATION OF POLYNUCLEAR HYDROCARBONS

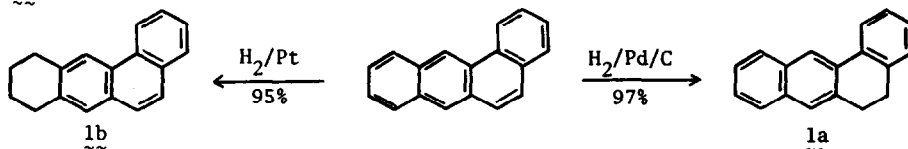
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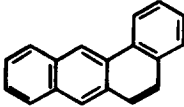
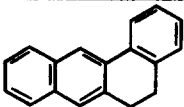
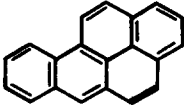
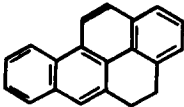
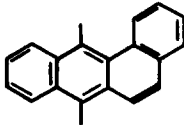
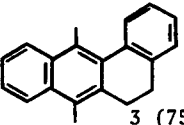
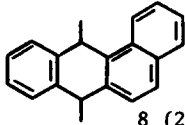
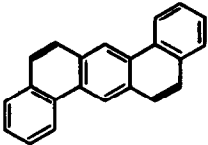
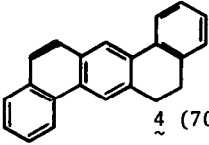
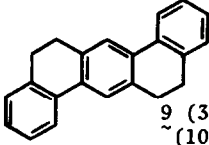
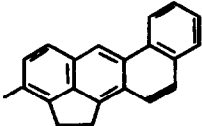
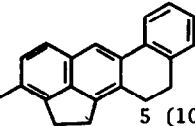
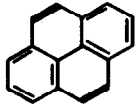
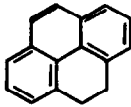
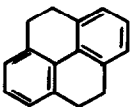
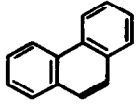
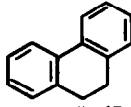
Reduction of polycyclic aromatic hydrocarbons (PAH) by alkali metals in liquid ammonia has been shown in prior studies<sup>1</sup> to be generally controllable to the dihydro stage, regiospecific, and predictable by molecular orbital theory. In contrast, catalytic hydrogenation of PAH is apparently neither controllable nor predictable, product structure being highly dependent upon catalyst and conditions<sup>2</sup>. We now wish to report the finding that hydrogenation of PAH over a Pd/C catalyst under mild conditions affords regiospecifically and in high yield the products of hydrogen addition to the K-region.<sup>3</sup>

Hydrogenation of a series of representative PAH was investigated under mild conditions chosen to minimize the secondary processes, e.g. disproportionation, isomerization, overreduction, assumed to be partially responsible for previous erratic results. Preliminary experiments established that addition of hydrogen to benz[a]anthracene (BA) in the presence of a Pd/C catalyst at 20 psig and ambient temperature took place smoothly and regiospecifically to furnish 5,6-dihydro-BA (1a) (97%), while reaction over a Pt catalyst gave 8,9,10,11-tetrahydro-BA (1b) (95%) and 7,12-dihydro-BA (1c) (5%).<sup>6</sup>



Hydrogenation of benzo[a]pyrene (BP), 7,12-dimethylbenz[a]anthracene (DMBA), dibenz[a,h]-anthracene (DBA), 3-methylcholanthrene (MC), pyrene, and phenanthrene over Pd/C under similar conditions furnished the corresponding K-region dihydro derivatives 2 - 7, respectively (Table I). Only in the case of DMBA was a non-K-region dihydroaromatic product, 7,12-dihydro-DMBA (8) detected accompanying the major product, 5,6-dihydro-DMBA (3). Partial hydrogenation beyond the dihydro stage was exhibited by two of the three hydrocarbons having a K-region in the primary product. Thus, BP furnished 4,5-dihydro-BP cleanly, while DBA and pyrene underwent partial conversion to 5,6,12,13-tetrahydro-DBA (9) and 4,5,9,10-tetrahydropyrene (10), respectively. The ratio of 4 to 9 was 2:1 after 5 hr, and conversion to 9 was complete in 24 hr. No attempt was made to optimize yields. However, the second stage was generally slower than the first, and it is likely that with appropriate control of conditions, particularly the mole ratio of hydrogen, reaction could be controlled to either the dihydro or the tetrahydro stage, as desired. No hexahydro or further hydrogenated products were detected.

Table I: Low Pressure (20 psig) Hydrogenation of PAH over 10% Pd/C

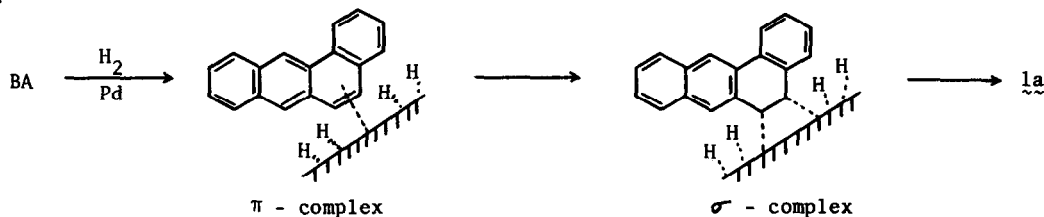
Hydrogenation <sup>a</sup>	Time, hr	Products <sup>b</sup> (Yield, %)
	10	 1 (97) <sup>c,d</sup>
	24	 2 (100) <sup>d</sup>
	8	 3 (75) <sup>d,e</sup> +  8 (25) <sup>d,f</sup>
	5 (24)	 4 (70) <sup>g</sup> +  9 (30) <sup>h</sup> (100) <sup>h</sup>
	18	 5 (100) <sup>j</sup>
	65 <sup>j</sup>	 6 (45) <sup>d</sup> +  10 (45) <sup>d</sup>
	120	 7 (70) <sup>d</sup>

<sup>a</sup>The K-region is indicated by a heavy bond. <sup>b</sup>Nmr spectra were in CCl<sub>4</sub>;  $\delta$  are relative to TMS. <sup>c</sup>Mp 94-95.5° (lit.<sup>9</sup> 148.5-149°);  $\delta$  3.26 (s,4,H<sub>4,5</sub>). <sup>d</sup>The nmr spectrum matched that of an authentic sample. <sup>e</sup>Mp 105-107° (lit.<sup>16</sup> 109°);  $\delta$  2.85 (s,4,H<sub>5,6</sub>). <sup>f</sup> $\delta$  4.05 (q,1,H<sub>7</sub>,J = 7), and 4.85 (q,1,H<sub>12</sub>,J = 7).<sup>17</sup> The isomers were separated by glpc on a 6 ft x 0.25 in OV 101 column; retention times matched those of authentic samples.<sup>16,17</sup> <sup>g</sup>Mp 194-195° (lit.<sup>15</sup> 193.5-194.5°);  $\delta$  3.10 (s,4,H<sub>5,6</sub>). <sup>h</sup>Mp 191-193 (lit.<sup>15</sup> 193.5-194.5°);  $\delta$  2.90 (s,8,H<sub>5,6,12,13</sub>). <sup>i</sup>Mp 154-155° (lit.<sup>14</sup> 154.5-155°);  $\delta$  2.95 (s,4,H<sub>11,12</sub>). <sup>j</sup>Pressure was 30 psig.

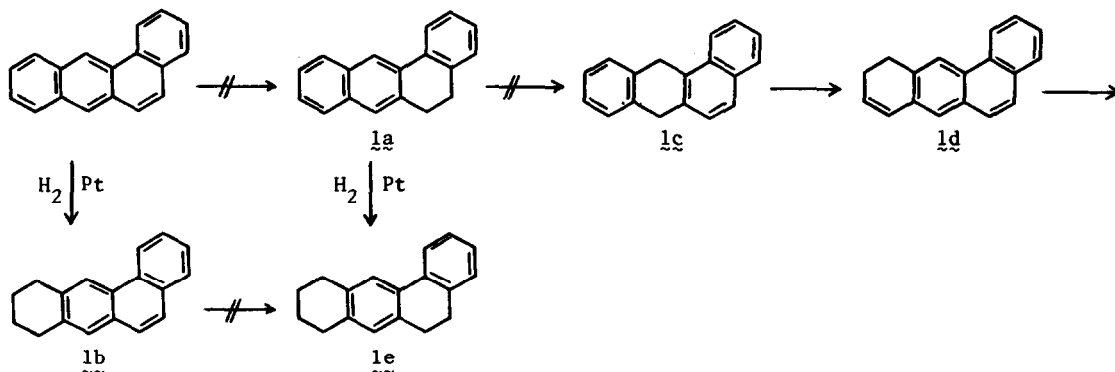
In a typical experiment, a solution of BP (2.0 g, 7.94 mmol) in ethyl acetate (35 ml) was stirred with 420 mg of 10% Pd/C under hydrogen (20 psig) at ambient temperature for 24 hr. The catalyst was removed by filtration through Celite, and washed with acetone. The filtrate was evaporated to dryness to afford 2.01 g (100%) of 4,5-dihydro-BP (**2**) as a white solid which crystallized from benzene-ethanol as white plates: mp 151-152° (lit.<sup>9</sup> 148.5-149°), nmr (CCl<sub>4</sub>) δ 3.26 (s, 4, benzylic), and 7.24-8.65 ppm (m, 10, aromatic). Tlc on silica gel impregnated with 2,4,7-trinitrofluorenone<sup>10</sup>, showed only one spot.

The observed regiospecific attack in the K-region is contrary to the theory proposed earlier by Hoiijtink.<sup>11</sup> According to the latter, electron transfer from the catalyst to the PAH occurs initially, followed by proton addition at the sites of maximum charge density in the resulting hydrocarbon negative ions under the influence of the homogenous electric field of the catalyst. For example, hydrogenation of BA is predicted to furnish **1c** and **1b**, rather than **1a** now found.

We propose that the mechanism of the reactions in Table I involves essentially concerted hydrogen addition from the catalyst to the electron-rich K-region bond, the region of minimum bond delocalization energy<sup>4,5</sup>, possibly proceeding *via* localized  $\pi$ - and  $\sigma$ - complexes. Reactions with OsO<sub>4</sub>, which are known to take place *via* a four center intermediate, also occur on this bond.<sup>5,12</sup>



This mechanism cannot adequately explain the products found with other catalysts and conditions. Thus, hydrogenation of BA over Pt gave, as confirmed herein, principally **1b**.<sup>6</sup> Similar reactions of BP<sup>9</sup>, DMBA<sup>13</sup>, MC<sup>14</sup>, and DBA<sup>15</sup> over Pt catalysts also furnished principally or exclusively non-K-region products in moderate yields. To test the possibility that these products arise *via* initial hydrogen addition in the K-region followed by catalyzed isomerization to thermodynamically favored non-K-region structures (e.g. **1a**  $\rightarrow$  **1c**  $\rightarrow$  **1d**  $\rightarrow$  **1b**), hydrogenation of **1a** over Pt was investigated and found to afford only **1e**. Under similar conditions **1b** remained



unchanged. Therefore,  $\underline{1b}$  is not an intermediate in the formation of  $\underline{1e}$ , and  $\underline{1a}$  is not an intermediate in the formation of  $\underline{1b}$  from BA. This was confirmed by reaction of BA with deuterium gas over Pt which gave  $^2\text{H}_4\text{-}\underline{1b}$  consistent with direct addition of four deuterium atoms in the terminal ring of BA and inconsistent with the alternative pathway through  $\underline{1a} \rightarrow \underline{1c} \rightarrow \underline{1d} + \underline{1b}$  which predicts net incorporation of approximately six deuterium atoms. It appears, therefore, that the reactions over Pt differ mechanistically from those over Pd.

Since low pressure hydrogenation over Pd provides high yields of products of predictable structure, the method appears to be of considerable synthetic utility. It complements metal-ammonia reduction which affords generally different dihydroaromatic products.<sup>1</sup>

Acknowledgement. This investigation was supported by grants CA 11968 and CA 19448 from the National Cancer Institute, DHEW.

#### References

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