Regioselective Catalytic Hydrogenation of Polycyclic Aromatic Hydrocarbons under Mild Conditions

Peter P. Fu, Hong M. Lee, and Ronald G. Harvey*

Ben May Laboratory, University of Chicago, Chicago, Illinois 60637

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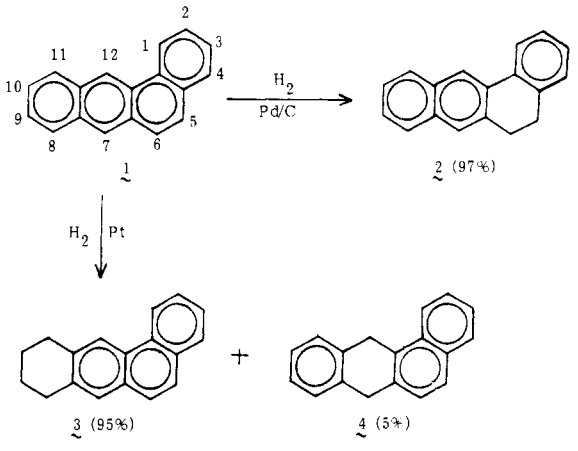
Hydrogenation of polynuclear hydrocarbons over a palladium catalyst at low pressure and ambient temperature affords regiospecifically the corresponding K-region dihydroarenes, while analogous reactions over a platinum catalyst take place regioselectively on terminal rings to provide the related tetrahydroarenes. Hydrogenation over palladium of phenanthrene, benz[*a*]anthracene, 7,12-dimethylbenz[*a*]anthracene, benzo[*a*]pyrene, 3-methylcholanthrene, dibenz[*a*,*h*]anthracene, and chrysene gave 9,10-dihydrophenanthrene, 5,6-dihydrobenz-[*a*]anthracene, 5,6-dihydro-7,12-dimethylbenz[*a*]anthracene, 4,5-dihydrobenzo[*a*]pyrene, 11,12-dihydro-3-methylcholanthrene, 5,6-dihydrodibenz[*a*,*h*]anthracene, and 5,6-dihydrochrysene, respectively (Table I). Hydrogenation over platinum of benz[*a*]anthracene, 7-methylbenz[*a*]anthracene, 12-methylbenz[*a*]anthracene, 7,12-dimethylbenz[*a*]anthracene, benzo[*a*]pyrene, chrysene, dibenz[*a*,*c*]anthracene, 5,6-dihydrobenz[*a*]anthracene, 5,6-dihydro-7,12-dimethylbenz[*a*]anthracene, and 4,5-dihydrobenzo[*a*]pyrene furnished the corresponding terminal ring tetrahydroarenes (Table II). Partial hydrogenation beyond the dihydro stage in the presence of palladium was exhibited only by hydrocarbons with more than one K region. In these cases, the second stage of hydrogen addition was generally slower than the first, so that the extent of reaction was readily controllable. Hydrogenation was blocked by alkyl substitution in an otherwise susceptible ring, and regioselectivity was diminished or abolished by increased hydrogen pressure, prolonged reaction, or acidity. The mechanism of reaction over palladium is proposed to involve concerted hydrogen addition to the K region, the region of minimum bond delocalization energy, preceded by localized π and/or σ complexes. Evidence is presented that hydrogenations over platinum do not involve initial addition to the K region followed by isomerization into the terminal ring. Instead, these reactions are suggested to involve addition of 2 mol of hydrogen via an intermediate π complex to the terminal ring which affords the most thermodynamically favored tetrahydroarene product, i.e., that which requires the minimum amount of energy for its formation.

Catalytic hydrogenation of polynuclear hydrocarbons, despite a long history of investigation,[1] has been for many years one of the least predictable and controllable reactions of these molecules. Recently however, in the course of synthetic studies aimed at the preparation of metabolites of carcinogenic polycyclic hydrocarbons, we observed regiospecific (or highly regioselective) hydrogenation of polycyclic hydrocarbons under mild conditions.[2,3] Reactions over a palladium/charcoal catalyst took place smoothly in the molecular K regions[4] to afford dihydroarenes,[2] while analogous reactions over a platinum catalyst occurred preferentially on terminal rings to provide the corresponding tetrahydroarenes.[3] For example, hydrogenation of benz[*a*]anthracene (**1**, BA) in the presence of a Pd/C catalyst at 20 psig of H_2 and ambient temperature gave 5,6-H_2BA (**2**, 97%), while an analogous reaction over a Pt catalyst furnished 8,9,10,11-H_4BA (**3**, 95%) and 7,12-H_2BA (**4**, 5%) (Scheme I).

Scheme I



We now report full details of our studies on the catalytic hydrogenation of polycyclic hydrocarbons under mild conditions.[2,3] A prime objective of this work was the development of convenient syntheses of partially hydrogenated hydrocarbon derivatives as potentially useful synthetic intermediates. One of the longstanding unsolved problems of polycyclic arene chemistry is the deficiency of methods for the functionalization of ring positions not susceptible to direct substitution. Since electrophilic, nucleophilic, and radical substitution reactions all occur regioselectively on a small fraction of the total ring positions, the majority of substituted polycyclic arenes are synthetically inaccessible except through tedious, individual, multistep synthesis from appropriately substituted

(1) Clar, E. "Polycyclic Hydrocarbons"; Academic Press: New York, 1964; Vol. I, II.
(2) Fu, P. P.; Harvey, R. G. *Tetrahedron Lett.* **1977**, 415.
(3) Fu, P. P.; Lee, H. M.; Harvey, R. G. *Tetrahedron Lett.* **1978**, 551.
(4) A K region is a bond, such as the 9,10-bond of phenanthrene, excision of which from a polynuclear hydrocarbon leaves an intact aromatic ring system.
(5) Pyrene (Ni, 300 °C, 80 atm of H_2) to 1,2,3,6,7,8-hexahydropyrene: Kagehira, K. *Bull. Chem. Soc. Jpn.*, **1931**, *6*, 241. Pyrene (Pd/C, 100 °C, 300 psig of H_2, $AlCl_3$, HCl) to 4,5-dihydropyrene (33%), 4,5,9,10-tetrahydropyrene (20%), 1,2,3,6,7,8-hexahydropyrene (27%), and perhydropyrene (4%): Aristoff, E.; Rieve, R. W.; Shalit, H. U.S. Patent 3 409 684, 1968.
(6) BA (Pt/Pd, $FeCl_2$, HCl) to **3** (77%): Fieser, L. F.; Hershberg, E. B. *J. Am. Chem. Soc.* **1937**, *59*, 2502; repetition in our laboratory with pure Pt gave **3** (80%), **4** (12%), and **5** (8%). BA (Pt/$SrCO_3$) to **2** (59%): Cho, H.; Harvey, R. G. *Tetrahedron Lett.* **1974**, 1491.
(7) BP (PtO_2, HOAc) to 7,8,9,10-H_4BP (37%) and 4,5-H_2BP (11%): Lijinsky, W.; Zechmeister, L. *J. Am. Chem. Soc.* **1953**, *75*, 5495.
(8) 3-MC (Pt/Pd,HOAc) to 6,7,8,9,10,12b-H_6-3-MC (40%) and 11,12-H_2-3-MC (20%): Fieser, L. F.; Hershberg, E. B. *J. Am. Chem. Soc.* **1938**, *60*, 940. 3-MC (Pt,HOAc) to 7,8,9,10-H_4-3-MC (no yield) and 11,12-H_2-3-MC (21%): Lijinsky, W.; Advani, G.; Keefer, L.; Ramahi, H.; Stack, L. *J. Chem. Eng. Data* **1972**, *17*, 100.
(9) 7,12-Me_2BA (Pd/$SrCo_3$) to 5,6-H_2-7,12-Me_2BA (59%): Hadler, H. I.; Kryger, A. C. *J. Org. Chem.* **1960**, *25*, 1896.
(10) Chrysene (Ni, 230 °C, 200 atm of H_2) to 1,2,3,4,-4a,7,8,9,10,11,12,12a-dodecahydrochrysene: Von Braun, J.; Irmisch, G. *Chem. Ber.* **1932**, *65*, 883.
(11) DBA (Pt,HOAc) to eight hydrogenated products including 1,2,3,4-H_4DBA (5%) and 5,6-H_2DBA (3%): Lijinsky, W. *J. Org. Chem.* **1961**, *26*, 3230.

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smaller molecular units.[1] The hydroaromatic compounds obtained on partial hydrogenation of polycyclic arenes may potentially undergo substitution in benzylic sites or in aromatic ring positions. Since these sites are likely to differ from those susceptible to substitution in the parent polycyclic hydrocarbon, certain of the less common isomeric substituted arenes are potentially accessible via the sequence hydrogenation, substitution, and dehydrogenation.

Results

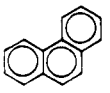
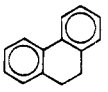
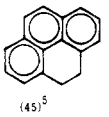
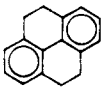
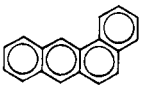
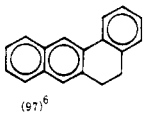
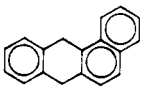
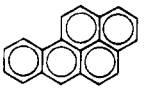
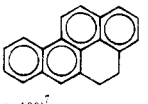
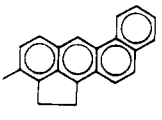
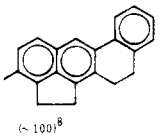
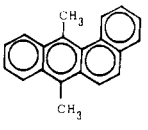
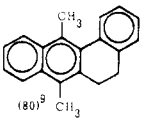
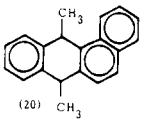
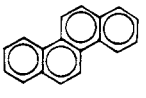
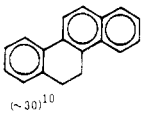
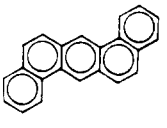
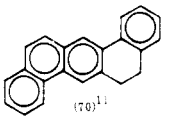
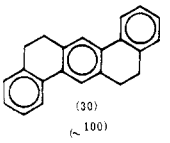
Hydrogenation of a series of representative polycyclic hydrocarbons was investigated under mild conditions chosen to minimize the secondary processes (disproportionation, isomerization, over reduction, etc.) assumed to be partially responsible for the complexity of products previously observed. At low pressure (20–50 psig) and ambient temperature, hydrogenation of these hydrocarbons in the presence of a palladium/charcoal catalyst furnished the products indicated in Table I. Since rates of hydrogen uptake varied considerably, reaction times were adjusted to favor good yields of the dihydroarenes. Addition of hydrogen to phenanthrene, BA, benzo[*a*]pyrene (BP), 3-methylcholanthrene (3-MC), and chrysene took place regiospecifically or highly regioselectively in the corresponding K regions to afford 9,10-dihydrophenanthrene, 5,6-H_2BA, 4,5-H_2BP, 11,12-H_2-3-MC, and 5,6-dihydrochrysene, respectively. In the case of 7,12-H_2BA, the K-region 5,6-dihydro derivative was accompanied by a lesser amount (20%) of the product of hydrogen addition in the meso region, 7,12-H_2-7,12-Me_2BA.

Partial hydrogenation beyond the dihydro stage was exhibited by four of the five hydrocarbons having more than one K region. In each case, addition of the second molar equivalent of hydrogen took place in the alternative K region. While BP afforded only 4,5-H_2BP, pyrene and dibenz[*a*,*h*]anthracene (DBA) underwent partial conversion to 4,5,9,10-tetrahydropyrene and 5,6,12,13-H_4DBA, respectively. Similarly, 7,8,9,10-H_4BP gave a mixture of the two isomeric hexahydro derivatives, 4,5,7,8,9,10-H_6BP and 7,8,9,10,11,12-H_6BP, plus a small amount (10%) of 4,5,7,8,9,10,11,12-H_8BP in an 18-h reaction. Conversion of 7,8,9,10-H_4BP to 4,5,7,8,9,10,11,12-H_8BP was complete in 48 h. In the case of DBA, the ratio of dihydro to tetrahydro compound was 2 after 5 h, and conversion to 5,6,12,13-H_4DBA was complete in 24 h. Hydrogenation of chrysene gave in addition to 5,6-dihydrochrysene a mixture of unidentified polysaturated products. No hexahydro or further hydrogenated products were detected in any of the other reactions. The second stage of these hydrogenations was generally slower than the first, and the extent of reaction could be controlled to yield predominantly the dihydro or tetrahydro products as desired with appropriate adjustment of the reaction time.

Hydrogenation in the K region was effectively blocked, however, by substitution in this molecular region. Thus, attempted hydrogenation of 9,10-diethylphenanthrene at 20 psig of H_2 failed to take place over a 24-h period. When hydrogen pressure was increased to 50 psig, a slow uptake of hydrogen (65 h) took place to provide 1,2,3,4-tetrahydro-9,10-diethylphenanthrene (64%) and 1,2,3,-4,5,6,7,8-octahydro-9,10-diethylphenanthrene (36%) as the sole isolable products.

The regioselectivity of these reactions was diminished or completely abolished under more vigorous conditions such as increased hydrogen pressure, prolonged reaction time, or the use of acidic cocatalysts. For example, hydrogenation of BA over the same Pd/C catalyst as employed in Table I at 50 psig of H_2 for 68 h gave a dramatically different product distribution consisting of **2**

Table I. Palladium-Catalyzed Hydrogenation of Polycyclic Hydrocarbons[a]

hydrocarbon	pressure, psig	time, h	products (yield, %)[b]
	20	120	 (70)
	50	65	 (45)[5]  (45)
	20	10	 (97)[6]  (3)
	20	24[c]	 (~100)[7]
	20	18[c]	 (~100)[8]
	20	8	 (80)[9]  (20)
	20	20[d]	 (~30)[10]
	20	5	 (70)[11]  (30)
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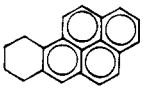
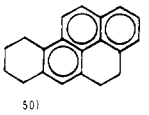
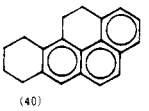
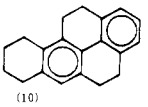
	45	18	 (50)  (40)
			 (10)
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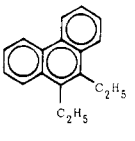
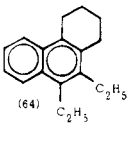
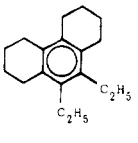
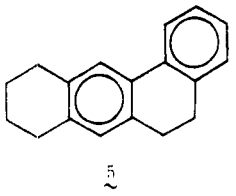
	50	65	 (64) 

[a] Reactions were conducted in ethyl acetate at ambient temperature. [b] References are to prior literature on the hydrogenation of the hydrocarbon (catalyst and conditions specified in parentheses) to give the products cited. [c] Reactions were probably complete in shorter time. [d] Details of this experiment were reported: Fu, P. P.; Harvey, R. G. *J. Org. Chem.* **1979**, *44*, 3778.

(26%), 4 (8%), and 5,6,8,9,10,11-H_6BA (5, 66%). Evi-



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dently, secondary hydrogenation of the initially formed 2 occurs under these relatively more drastic conditions. Similar reaction with acetic acid as cosolvent furnished an even more complex mixture containing more than four products.

The observed remarkable regioselectivity for K-region attack documented in Table I correlates with the olefinic character of the bonds in this molecular region which tend to be more localized than other aromatic bonds according to theoretical calculations.[12] Although no attempt was made to determine the rates of hydrogen addition, they appear to correlate approximately with the theoretically calculated electron densities in the K regions.[12] Also, the observed greater facility of hydrogenation of the parent hydrocarbons relative to their dihydro products is consistent with the theoretical expectation based on the anticipated generally greater bond delocalization energies of the secondary over the primary K-region bonds.

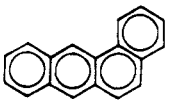
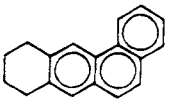
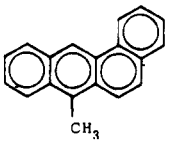
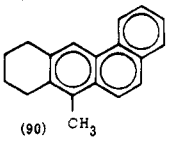
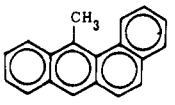
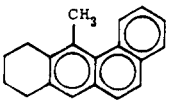
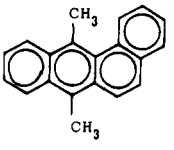
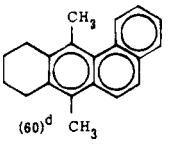
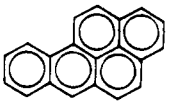
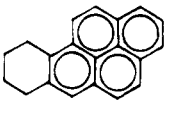
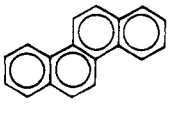
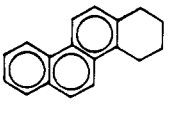
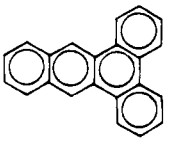
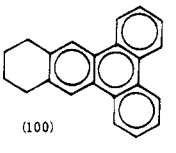
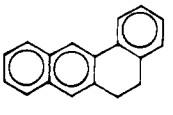
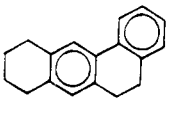
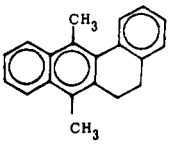
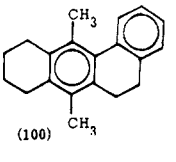
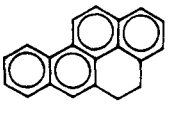
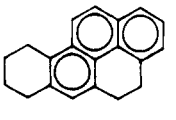
The potent carcinogenic hydrocarbons BP, 7,12-H_2BA, DBA, and 3-MC were observed to undergo efficient hydrogenation at lower pressures and in shorter times than the inactive or weakly carcinogenic hydrocarbons phenanthrene, pyrene, BA, and chrysene. While this accords with the Pullman theory of carcinogenesis which predicts exceptional reactivity in the K regions of carcinogenic hydrocarbons,[12] the correlation would appear fortuitous since there is now strong evidence that metabolic activation occurs in non-K regions to furnish reactive diol epoxides which are the principal, ultimate, active carcinogens.[13]

Analogous hydrogenations conducted in the presence of a platinum catalyst took place regioselectively on terminal rings to afford the corresponding tetrahydroarenes as the principal products. Thus, hydrogenation of BA, 7-MeBA, 12-MeBA, 7,12-Me_2BA, BP, chrysene, and dibenz[*a*,*c*]-anthracene in ethyl acetate over a platinum catalyst at ambient temperature and at 40–50 psig pressure of hydrogen furnished regioselectively and in good yield the related tetrahydroarenes indicated in Table II. Similarly, hydrogenation of the K-region dihydro derivatives of BA, 7,12-Me_2BA, and BP under these conditions provided the corresponding hexahydro derivatives 5,6,8,9,10,11-H_6BA, 7,12-Me_2-5,6,8,9,10,11-H_6BA, and 4,5,7,8,9,10-H_6BP, respectively. In contrast, hydrogenation of triphenylene under similar conditions afforded a mixture of 1,2,3,4-tetrahydro-, 1,2,3,4,5,6,7,8-octahydro-, and 1,2,3,-4,5,6,7,8,9,10,11,12-dodecahydrotriphenylenes (6–8) in the ratio of 7:4:3.

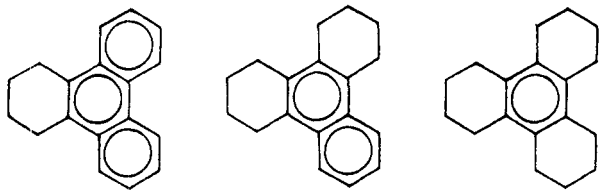
Hydrogenations over platinum required somewhat higher hydrogen pressures and longer reaction periods for comparable extents of reaction than for the analogous reactions over a palladium catalyst. This may partially account for the somewhat diminished regioselectivity and tendency to proceed beyond the tetrahydro stage of the

(12) Pullman, A.; Pullman, B. *Adv. Cancer Res.* **1955**, *3*, 117.
(13) Reviews: Harvey, R. G. In "Safe Handling of Chemical Carcinogens, Mutagens, Teratogens and Highly Toxic Substances"; Walters, D. B., Ed.; Ann Arbor Science Publishers: Ann Arbor, MI, 1980; Vol. 2, p 439. Harvey, R. G.; Fu, P. P. In "Polycyclic Hydrocarbons and Cancer"; Gelboin, H. V., Ts'o, P. O. P., Eds.; Academic Press: New York, 1978; Vol. I, p 133.

Table II. Platinum-Catalyzed Hydrogenation of Polycyclic Hydrocarbons[a]

hydrocarbon	tetrahydroarene (yield, %)
	 (95)[b]
	 (90)
	 (65)[c]
	 (60)[d]
	 (86)
	 (42)[e]
	 (100)
	 (85)
	 (100)
	 (25)

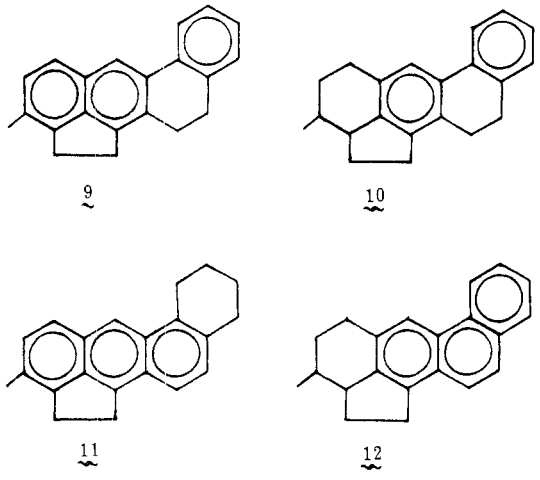
[a] Experimental details are found in the Experimental Section. Minor products obtained are listed in the footnotes. [b] 7,12-H_2BA (5%). [c] 7,12-H_2-12-Me_2BA (10%) and 5,6,8,9,10,11-H_6BA (25%). [d] Four minor products were detected by TLC but were not identified. [e] Details of this experiment were reported: Fu, P. P.; Harvey, R. G. *J. Org. Chem.* **1979**, *44*, 3778.



6 7 8

former. The yields reported in Table II are not necessarily optimum but are only the best attained from several exploratory runs with varying times and conditions.

Inhibition of hydrogenation by alkyl substitution was observed in the case of 11,12-H_2-3-MC (**9**) which failed to



9 10 11 12

add hydrogen in the presence of a platinum catalyst to provide the hexahydro derivative **10**, analogous to **5**. This is consistent with the reported[14] hydrogenation of 3-MC over a platinum catalyst to furnish 7,8,9,10-H_4-3-MC (**11**) rather than the terminal ring tetrahydro isomer 2a,3,4,5-H_4-3-MC (**12**).

Separation of the mixtures of hydrogenated products encountered in these studies, often exceedingly difficult by conventional chromatographic methods, was efficiently accomplished in most cases by the technique of "charge-transfer chromatography".[15] Columns (or TLC plates) of silica gel or Florisil impregnated with 2% trinitrofluorenone were utilized for this purpose. Migration of compounds was visualized by the distinctive colors of the individual charge-transfer complexes.

Discussion

It is clear that catalytic hydrogenation of polynuclear hydrocarbons is both controllable and predictable under appropriately mild conditions. Reactions over a palladium catalyst at low pressures and temperatures afford regiospecifically the corresponding K-region dihydroarenes, while analogous reactions over a platinum catalyst take place preferentially on terminal rings to furnish the related tetrahydroarenes. The remarkable regioselectivity of these reactions contrasts with the relatively complex mixtures of polyhydrogenated products commonly reported in the prior literature.[1,5-11] In the majority of these earlier examples, more strenuous conditions of pressure and temperature or acidic media were employed, and in many cases the catalysts were contaminated with other metals. For example, Fieser[6] employed an Adams catalyst containing a small percentage of palladium and conducted hydro-

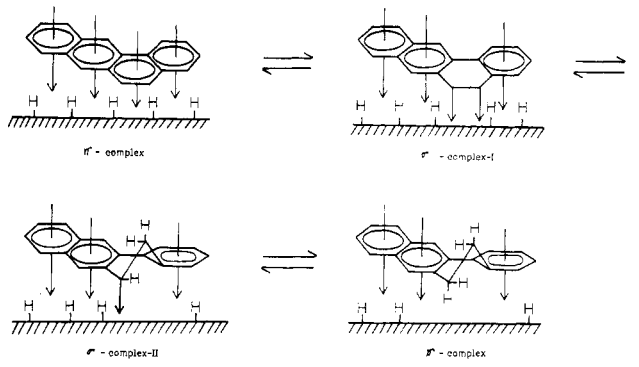
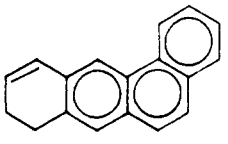


Figure 1. Proposed mechanism of palladium-catalyzed hydrogenation in the K region of polycyclic arenes.

genations of polycyclic hydrocarbons in the presence of $FeCl_2$ and HCl to enhance the rate of hydrogen uptake. In our experience, although the rates of hydrogenations are enhanced by the presence of acids, the complexity of the product mixtures also increases.

The mechanisms of these reactions appear distinctively different for these two catalyst systems. Since it is conceivable that the terminal-ring tetrahydroarenes formed over platinum arise via initial hydrogen addition in the K regions followed by catalyzed isomerization to thermodynamically favored non-K-region structures (e.g., **1** → **2** → **4** → **13** → **3**), hydrogenation of **2** over platinum was in-



13

vestigated and found to afford only **5** and no trace of **4**, **13**, or **3**. Since **5** could conceivably be formed from **3**, hydrogenation of **3** under similar conditions was also tested, and **3** was recovered unchanged. Therefore, 5,6-H_2BA is not an intermediate in the platinum-catalyzed hydrogenation of BA to 8,9,10,11-H_4BA. It appears, therefore, that platinum-catalyzed hydrogenations differ mechanistically from their palladium-catalyzed counterparts.

The mechanism of hydrogenation over palladium we propose involves essentially concerted hydrogen addition from the catalyst to the electron-rich, K-region bond, the region of minimum bond delocalization energy, preceded by localized π and σ complexes (Figure 1). It is likely that simultaneous association of the aromatic ring system with the catalyst surface assists the reaction by lowering the energy of the transition state. This mechanism is essentially the Langmuir–Hinshelwood mechanism.[16,17] The Rideal mechanism,[17,18] in which only the substrate is chemisorbed on the catalyst and the hydrogen comes from the gas phase, is equally consistent with most of the findings. However, the inhibition of hydrogen addition to the 9,10-positions of phenanthrene by ethyl substitution in this region is more simply explicable in terms of cis addition from the catalyst surface (Figure 1) than by backside addition.

The mechanism of platinum-catalyzed hydrogenation in terminal rings is obviously quite different. The terminal

(14) Lijinsky, W.; Adrani, G.; Keefer, L.; Ramahi, H. Y.; Stack, L. *J. Chem. Eng. Data* **1972**, *17*, 100.
(15) Harvey, R. G.; Halonen, M. *J. Chromatogr.* **1966**, *25*, 294.
(16) Linstead, R. P.; Doering, W. E.; Davis, S. B.; Levin, P.; Whetstone, R. R. *J. Am. Chem. Soc.* **1942**, *64*, 1985.
(17) Laidler, K. J. In "Catalysis"; Van Nostrand-Reinhold: New York 1954; Vol. I, pp 128–151. Smith, H. A. *Ibid.* 1957; Vol. V, p 183.
(18) Farina, M.; Morandi, C.; Mantica, E.; Botta, D. *J. Chem. Soc., Chem. Commun.*, **1976**, 816.

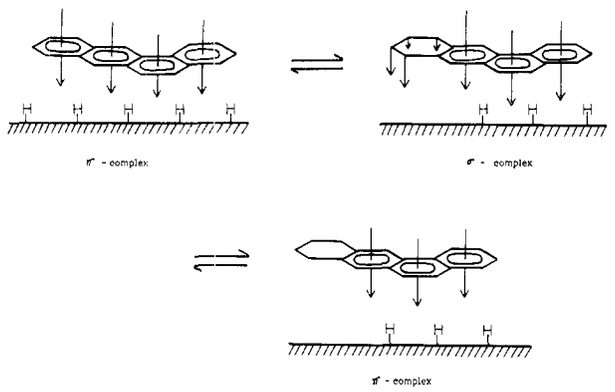
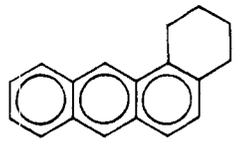


Figure 2. Proposed mechanism of platinum-catalyzed hydrogenation in terminal rings of polycyclic arenes. It is likely that the four hydrogen atoms add sequentially.

rings are not normally susceptible to electrophilic, nucleophilic, or radical reactions. Consideration of product structure indicates that the terminal ring which undergoes hydrogen addition is in all cases the one which affords the most thermodynamically favored product, i.e., that which requires a minimum of energy for its formation. Thus, hydrogenation of BA over platinum gives 8,9,10,11-H_4BA (**3**), and not 1,2,3,4-H_4BA (**14**). Formation of **3**, which



14

retains the phenanthrene structural unit, requires approximately 8 kcal less energy than formation of **14** which contains the anthracene structural component.[19] We propose that these low-pressure hydrogenations over platinum involve initial π complexation between the catalyst and two or more aromatic bonds followed by preferential σ complexation in the most energetically favorable molecular region and hydrogen addition in this ring to afford the most thermodynamically favored tetrahydroarene product (Figure 2). Since the aromatic ring which undergoes addition of hydrogen tends to also be the least sterically crowded, it is conceivable that steric considerations may also play a role. While this cannot be ruled out, it should be noted that hydrogenation of 7-MeBA takes place exclusively in the relatively crowded D ring (i.e., in the 8, 9, 10, and 11 positions), suggesting that product structure is relatively insensitive to steric crowding.

From a purely synthetic viewpoint, the catalytic hydrogenation methods described herein provide the most convenient synthetic routes to the K-region- and terminal-ring-hydrogenated derivatives of polycyclic hydrocarbons. Prior studies have established that reduction of polycyclic hydrocarbons by alkali metals in liquid ammonia is also regiospecific, and the products are predictable by molecular orbital theory.[20] Since metal–ammonia reduction generally provides different hydroaromatic products than those obtained from either Pd- or Pt-catalyzed hydrogenation,[21] the three methods are complementary. In principle, they can be utilized in any combination to synthesize virtually any polycyclic, hydroaromatic isomer desired.

Experimental Section

General Methods. The NMR spectra were obtained on a Varian T-60 or a Bruker HX-270 spectrometer with tetramethylsilane as internal standard in either CCl_4 or $CDCl_3$; integration was consistent with all assignments. Gas chromatographic analyses were performed on a Varian 2700 chromatograph employing a 6.0 ft × 0.25 in., 10% OV-101 on 60–70-mesh Anakrom AS support column at 225–300 °C.

Platinum(IV) oxide, 10% platinum/charcoal, and 10% palladium/charcoal catalysts were purchased from Ventron Corp. 3-Methylcholanthrene, dibenz[*a*,*h*]anthracene, 7,12-dimethylbenz[*a*]anthracene, and 2,4,7-trinitrofluorenone (TNF) were purchased from Eastman Chemical Co. Dibenz[*a*,*c*]anthracene,[22] 9,10-diethylphenanthrene,[23] 7,12-dihydrobenz[*a*]anthracene,[20,24] and 7,8,9,10-tetrahydrobenzo[*a*]pyrene[25] were prepared by the procedures previously described. Other polycyclic hydrocarbons were obtained from commercial sources and were purified by recrystallization as necessary. All new compounds gave satisfactory microanalyses for C and H within ±0.3% and/or mass spectra consistent with the assigned structure.

General Procedure for Catalytic Hydrogenation. Hydrogenation experiments were conducted in a Vortex low-pressure hydrogenator manufactured by J. B. Thompson Co. Reactions were conducted in a 500-mL Pyrex bottle with ethyl acetate as solvent unless otherwise specified. The substrate, metal catalyst, and solvent(s) were introduced into the reaction vessel which was flushed three times with hydrogen gas before being pressurized. Reactions were stirred magnetically at moderate speed. The crude reaction products were filtered through Celite with several acetone washes, evaporated to dryness, taken up in hexane or other appropriate solvent, and purified by passage through a short column of Florisil.

Hydogenations over Palladium (Table I). Reactions were carried out in ethyl acetate over a 10% Pd/C catalyst at ambient temperature and at the pressure and for the reaction period specified in Table I. The quantities of the hydrocarbon, catalyst, and solvent employed are listed in order in parentheses following the name of the hydrocarbon.

(a) Benzo[*a*]pyrene (2.0 g, 7.9 mmol; 420 mg; 35 mL). Workup gave 4,5-dihydrobenzo[*a*]pyrene (2.01 g, 100%) as a white solid: mp 142–143 °C (benzene–hexanes) (lit.[7,26] mp 143–144 °C; 148.5–149 °C); NMR (CCl_4) δ 3.38 (s, 4, benzylic), 7.40–8.12 (m, 8, aromatic), 8.72–8.89 (m, 2, $H_{10,11}$); a single spot was detected on TLC on silica gel impregnated with TNF.[15]

(b) 3-Methylcholanthrene (120 mg, 0.45 mmol; 35 mg; 25 mL). 3-Methyl-11,12-dihydrocholanthrene was obtained in essentially quantitative yield as colorless plates: mp 154–155 °C (benzene–hexanes) (lit.[27] mp 154.5–155 °C); NMR ($CDCl_3$) δ 2.40 (s, 3, CH_3), 2.93 (s, 4, $H_{11,12}$), 3.33 (apparent s, 4, $H_{1,2}$), 7.10–8.15 (m, 7, aromatic).

(c) Benz[*a*]anthracene (180 mg, 0.79 mmol; 40 mg; 15 mL). NMR and GLC analyses of the crude product indicated the presence of 5,6-dihydrobenz[*a*]anthracene (**2**, ~97%) and 7,12-dihydrobenz[*a*]anthracene (**4**, ~3%). Crystallization from

(19) The differences between the empirical resonance energies of benz[*a*]anthracene and phenanthrene and anthracene are 28.1 and 20.3 kcal, respectively; therefore, formation of **3** is favored over **14** by 7.8 kcal. Streitwieser, A., Jr. "Molecular Orbital Theory for Organic Chemists"; Wiley: New York, 1961; p 241.

(20) Harvey, R. G. *Synthesis* **1970**, 161. Harvey, R. G. *J. Org. Chem.* **1971**, *36*, 3306. Lindow, D. F.; Cortez, C.; Harvey, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 5406. Harvey, R. G.; Lindow, D. F.; Rabideau, P. W. *Ibid.* **1972**, *94*, 5412. Harvey, R. G.; Lindow, D. F.; Rabideau, P. W. *Tetrahedron* **1972**, *28*, 2909. Harvey, R. G.; Fu, P. P.; Rabideau, P. W. *J. Org. Chem.* **1976**, *41*, 2706.

(21) For example, reduction of BA with lithium in ammonia affords 7,12-H_2BA (**4**) as the principal product (Harvey, R. G.; Urberg, K. *J. Org. Chem.* **1968**, *33*, 2206), whereas catalytic hydrogenation of BA over palladium or platinum catalysts provides 5,6-H_2BA (**2**) or 8,9,10,11-H_4BA (**3**), respectively. 1,2,3,4-H_4BA was synthesized in two steps from reduction of BA with sodium and alcohol to 1,2,3,4,7,12-H_6BA followed by dehydrogenation with DDQ (Fu, P. P.; Cortez, C.; Sukumaran, K. B.; Harvey, R. G. *J. Org. Chem.* **1979**, *44*, 4265).

(22) Harvey, R. G.; Leyba, C.; Konieczny, M.; Fu, P. P.; Sukumaran, K. B. *J. Org. Chem.* **1978**, *43*, 3423.

(23) Rabideau, P. W.; Harvey, R. G. *J. Org. Chem.* **1970**, *35*, 25.

(24) Harvey, R. G.; Urberg, K. *J. Org. Chem.* **1968**, *33*, 2206.

(25) Kon, G. A.; Roe, E. M. *J. Chem. Soc.* **1945**, 143.

(26) Yagi, H.; Holder, P. M.; Dansette, P. M.; Hernandez, O.; Hey, H. J. C.; LeMahieu, R. A.; Jerina, D. M. *J. Org. Chem.* **1976**, *41*, 977.

(27) Fieser, L. F.; Hershberg, E. B. *J. Am. Chem. Soc.* **1938**, *60*, 940.

methanol gave pure **2**: mp 94–95.5 °C (lit.[28] mp 96–96.5 °C); NMR (CCl_4) δ 2.95 (s, 4, $H_{5,6}$), 7.07–8.10 (m, 10, aromatic). Pure **4** was collected from the GLC column: NMR (CCl_4) δ 4.05–4.36 (m, 2, H_7), 4.30–4.48 (m, 2, H_{12}), 7.0–7.68 (m, 10, aromatic), in good agreement with reported values.[21] Larger scale reactions tended to afford higher percentages of **4**, to a maximum of 10%. In these cases, purification of the crude product was most conveniently accomplished by taking advantage of the greater ease of oxidation of **4** with sodium dichromate as described.[28] Prolongation of the reaction time, an increased pressure, or an increased ratio of the catalyst tended to provide products of further hydrogenation, notably 5,6,8,9,10,11-hexahydrobenz[*a*]anthracene (**5**). For example, hydrogenation of 500 mg of benz[*a*]anthracene over 250 mg of 10% Pd/C in ethyl acetate (30 mL) at 50 psig of H_2 for 68 h gave **2** (26%), **4** (8%), and **5** (66%). The NMR spectrum of the latter, obtained as an oil, was identical with that of an authentic sample whose synthesis is described in a later paragraph.

(d) 7,12-Dimethylbenz[*a*]anthracene (500 mg, 1.95 mmol; 120 mg; 20 mL). NMR spectral analysis of the crude product indicated the presence of 7,12-dimethyl-5,6-dihydrobenz[*a*]-anthracene (80%) and *cis*-7,12-dihydro-7,12-dimethylbenz[*a*]-anthracene (20%). The former was isolated upon crystallization from benzene–hexane as light yellow prisms: mp 112–113 °C (lit.[9] mp 112–113 °C); NMR (CCl_4) δ 2.60 (s, 3,7-CH_3), 2.67–2.98 (m, 4, $H_{5,6}$), 2.87 (s, 3, 12-CH_3), 7.02–8.17 (m, 8, aromatic).

(e) Dibenz[*a*,*h*]anthracene (270 mg, 1.2 mmol; 80 mg; 25 mL). NMR spectral analysis of the product showed 5,6-dihydrodibenz[*a*,*h*]anthracene (5%) and 5,6,12,13-tetrahydrodibenz[*a*,*h*]anthracene (95%). The latter crystallized from benzene–methanol as pale yellow plates: yield 75%; mp 191–193 °C (lit.[11] mp 193.5–194.5 °C); NMR (CCl_4) δ 2.91 (s, 8, benzylic), 7.07–7.80 (m, 10, aromatic). 5,6-Dihydrodibenz[*a*,*h*]anthracene was collected from the mother liquor by preparative GLC and crystallized from benzene–methanol as a pale yellow solid: mp 194–195 °C (lit.[11] mp 194–195 °C); NMR (CCl_4) δ 2.98–3.22 (m, 4, $H_{5,6}$), 7.12–9.10 (m, 12, aromatic). A similar reaction for 7 h instead of 24 h gave the dihydro and tetrahydro derivatives in 63 and 7% yields, respectively, and unreacted dibenz[*a*,*h*]-anthracene (30%).

(f) Pyrene (1.0 g, 4.95 mmol; 250 mg; 20 mL). NMR and GLC analyses of the product showed 4,5-dihydropyrene (45%), 4,5,9,10-tetrahydropyrene (45%), and pyrene (10%). Products were collected from the GLC column and characterized by comparison of their NMR spectra with those of authentic samples prepared by reduction of pyrene with lithium in ammonia:[29] NMR of 4,5-dihydropyrene δ 3.35 (s, 4, $H_{4,5}$), 7.10–8.18 (m, 8, aromatic); NMR of 4,5,9,10-tetrahydropyrene δ 2.90 (s, 8, benzylic), 7.10 (apparent s, 6, aromatic).

(g) Phenanthrene (600 mg, 3.4 mmol; 200 mg; 20 mL). NMR and GLC analyses in comparison with authentic samples showed 9,10-dihydrophenanthrene (70%) and recovered phenanthrene (30%).

(h) 9,10-Diethylphenanthrene (234 mg, 1 mmol; 170 mg; 20 mL). The NMR spectrum of the product showed the presence of two components subsequently identified as 9,10-diethyl-1,2,3,4-tetrahydrophenanthrene (64%) and 9,10-diethyl-1,2,3,4,5,6,7,8-octahydrophenanthrene (36%). These two products were separated by chromatography on a column of Florisil impregnated with 2% TNF.[15] Elution with hexane initially gave the octahydro compound as silky needles: mp 104–105 °C (acetone–hexane); NMR (CCl_4) δ 1.07 (t, 6, CH_3, J = 7.5 Hz), 1.56–1.93 (m, 8, $H_{2,3,6,7}$), 2.30–2.80 (m, 12, $H_{1,4,5,8}$ and CH_2). Further elution with hexane provided the tetrahydro compound as an oil: NMR (CCl_4) δ 1.07 (t, 6, CH_3, J = 7.5 Hz), 1.56–1.93 (m, 4, $H_{2,3}$), 2.30–2.80 (m, 8, H_{14} and CH_2), 6.98–7.78 (m, 4, aromatic).

(i) 7,8,9,10-Tetrahydrobenzo[*a*]pyrene (120 mg, 0.47 mmol; 60 mg; 15 mL). 4,5,7,8,9,10,11,12-Octahydrobenzo[*a*]pyrene was obtained in essentially quantitative yield as pale yellow plates: mp 93–94 °C (benzene–hexane); NMR (CCl_4) δ 1.60–1.92 (m, 4, $H_{8,9}$), 2.47–2.85 (m, 4, $H_{7,10}$), 2.78 (s, 8, $H_{4,5,11,12}$), 6.70 (s, 1, H_6), 6.94 (s, 3, H_{1-3}). In a second experiment in which reaction time was shortened from 48 to 24 h there were obtained the intermediate 4,5,7,8,9,10-hexahydro- and 7,8,9,10,11,12-hexahydrobenzo[*a*]pyrenes (12 and 25%, respectively) along with the octahydro compound (63%). These two isomers could not be separated even by "charge-transfer chromatography" on a TNF column.[15] The NMR spectral pattern of 4,5,7,8,9,10-hexahydrobenzo[*a*]pyrene in the mixture was identical with that of an authentic sample, the synthesis of which is described below. The NMR spectrum of 7,8,9,10,11,12-hexahydrobenzo[*a*]pyrene showed the following shifts: δ 1.8–2.2 (m, 4, $H_{8,9}$), 3.1–3.4 (m, 4, $H_{7,10}$), 3.2 (s, 4, $H_{11,12}$), 7.3–8.1 (m, 6, aromatic). In a similar experiment conducted for 18 h the 4,5,7,8,9,10-hexahydro and 7,8,9,10,11,12-hexahydro isomers were obtained in 40 and 50% yields, respectively, while the octahydro compound was formed to the extent of only 10%.

Hydrogenations over Platinum. Reactions were conducted in ethyl acetate (except as otherwise noted) over a 10% Pt/C or a PtO_2 catalyst at ambient temperature. The catalyst, pressure, reaction time, and the quantities of the hydrocarbon, catalyst, and solvent employed are indicated in order in parentheses for each hydrocarbon listed.

(a) Benz[*a*]anthracene (PtO_2; 50 psig; 44 h; 2.0 g, 8.8 mmol; 400 mg; 30 mL). Analysis of the product by GLC and NMR indicated it to be a mixture of 8,9,10,11-tetrahydrobenz[*a*]-anthracene (**3**, 95%) and 7,12-dihydrobenz[*a*]anthracene (**4**, 5%). Crystallization from acetone–methanol gave **3** as white needles: mp 88–89 °C (lit.[30] mp 88.5–89.5 °C); NMR (CCl_4) δ 1.50–2.10 (m, 4, $H_{9,10}$), 2.52–3.17 (m, 4, $H_{8,11}$), 7.07–7.85 (m, 6, aromatic), 8.25 (s, 1, H_{12}), 8.36–8.63 (m, 1, H_1).

Hydrogenation of **1** was also carried out under the acidic conditions employed by Fieser[6] (PtO_2; 20 psig; 4 h; 500 mg, 2.2 mmol; 50 mg; 25 mL + 3 mL of 0.1% $FeCl_2 \cdot H_2O$ in concentrated HCl; see Hydrogenations over Platinum). Analysis of the product by GLC and NMR indicated the presence of **1** (18%), **3** (9%), **4** (58%), and 5,6,8,9,10,11-hexahydrobenz[*a*]anthracene (**5**, 15%).

(b) 7,12-Dimethylbenz[*a*]anthracene (7,12-Me_2BA) (PtO_2; 50 psig; 22 h; 300 mg, 1.2 mmol; 85 mg; 20 mL). GLC and NMR analyses showed the product to consist of 8,9,10,11-H_4-7,12-Me_2BA (64%), *cis*-7,12-H_2-7,12-Me_2BA[31] (18%), 5,6-H_2-7,12-Me_2BA (12%), and 5,6,8,9,10,11-H_6-7,12-Me_2BA (6%) in comparison with authentic samples of these compounds. Crystallization from benzene–methanol gave pure 8,9,10,11-H_4-7,12-Me_2BA: mp 115–116 °C (lit.[32] mp 114–116 °C); NMR (CCl_4) δ 1.72–2.02 (m, 4, $H_{9,10}$), 2.53 (s, 3, 7-CH_3), 2.81 (s, 3, 12-CH_3), 2.72–3.08 (m, 4, $H_{8,11}$), 7.05–7.95 (m, 5, H_{2-6}), 8.35–8.63 (m, 1, H_1).

Analogous hydrogenation of 7,12-Me_2BA in the presence of added acetic acid (PtO_2; 30 psig; 22 h; 25 mg; 50 mg; 15 mL + 0.2 mL of HOAc) afforded a more complex product mixture: 5,6,8,9,10,11-H_6-7,12-Me_2BA (55%), *cis*-7,12-H_2-7,12-Me_2BA[31] (19%), *trans*-7,12-H_2-7,12-Me_2BA[33] (10%), 5,6-H_2-7,12-Me_2BA (6%), and 8,9,10,11-H_4-7,12-Me_2BA (10%). Hydrogenation of 7,12-Me_2BA under the acidic conditions of Fieser[6] (PtO_2; 20 psig; 24 h; 50 mg; 100 mg; 20 mL of 1% $FeCl_2 \cdot H_2O$ in concentrated HCl) also afforded complex hydrogenated products: 5,6,8,9,10,11-H_6-7,12-Me_2BA (62%), *cis*-7,12-H_2-7,12-Me_2-BA (15%), *trans*-7,12-H_2-7,12-Me_2BA (6%), 5,6-H_2-7,12-Me_2BA (11%), and 8,9,10,11-H_4-7,12-Me_2BA (6%).

(c) 7-Methylbenz[*a*]anthracene (10% Pt/C; 50 psig; 40 h; 1.0 g, 4.1 mmol; 200 mg; 20 mL). The crude product showed one strong spot and four weak spots on TLC on a 2% TNF on Florisil plate. Crystallization from methanol gave pure 7-methyl-8,9,10,11-tetrahydrobenz[*a*]anthracene (540 mg, 53%) as white plates: mp 73–75 °C (lit.[29] mp 73.9–74.7 °C); NMR (CCl_4) δ 1.58–2.02 (m, 4, $H_{9,10}$), 2.50 (s, 3, CH_3), 2.53–2.70 (m, 4, $H_{8,11}$), 7.02–8.01 (m, 5, aromatic), 8.20 (s, 1, H_{12}), 8.03–8.66 (m, 1, H_1).

(d) 12-Methylbenz[*a*]anthracene (10% Pt/C; 50 psig; 17 h; 1.0 g, 4.1 mmol; 290 mg; 20 mL). GLC and NMR analyses showed the product to contain 12-methyl-8,9,10,11-tetrahydrobenz[*a*]anthracene (65%), 5,6,8,9,10,11-hexahydro-12-methylbenz[*a*]anthracene (25%), and 7,12-dihydro-12-methylbenz[*a*]-anthracene (10%). Crystallization from methanol gave 12-

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methyl-8,9,10,11-tetrahydrobenz[a]anthracene as colorless rhombic crystals: mp 103–104 °C; NMR ($CDCl_3$) δ 1.68–2.15 (m, 4, $H_{9,10}$), 2.65–3.15 (m, 4, $H_{8,10}$), 2.90 (s, 3, CH_3), 7.33–8.00 (m, 6, aromatic), 8.60 (m, 1, H_1).

(e) Dibenz[a,c]anthracene (10% Pt/C; 40 psig; 17 h; 1.0 g, 3.6 mmol; 200 mg; 30 mL). The product isolated in essentially quantitative yield was identified as 10,11,12,13-tetrahydrodibenz[a,c]anthracene: mp 201–203 °C (benzene–hexane) (lit.[32] mp 198–199 °C); NMR ($CDCl_3$) δ 1.5–2.15 (m, 4, $H_{11,12}$), 2.81–3.21 (m, 4, $H_{10,13}$), 7.45–7.77 (m, 4, $H_{2,3,6,7}$), 8.25 (s, 2, $H_{9,14}$), 8.40–8.83 (m, 4, $H_{1,4,5,8}$).

(f) Triphenylene (PtO_2; 35 psig; 48 h; 725 mg, 3.2 mmol; 260 mg; 20 mL). The white solid product (730 mg) was separated by chromatography on a column of Florisil impregnated with 2% TNF.[15] Elution with hexanes gave 1,2,3,4,5,6,7,8,9,10,11,12-dodecahydrotriphenylene: 83 mg (12%); mp 233–234 °C (acetone–hexane) (lit.[34] mp 232–233 °C); NMR (CCl_4) δ 1.48–1.98 (m, 12, benzylic), 1.20–1.70 (m, 12, methylene). Further elution with hexanes gave 1,2,3,4,5,6,7,8-octahydrotriphenylene: 120 mg (16%); mp 127–129 °C (lit.[35] mp 129–130 °C); NMR (CCl_4) δ 1.40–2.15 (m, 8, $H_{2,3,6,7}$), 2.30–2.78 (m, 4, $H_{4,5}$), 2.80–3.18 (m, 4, $H_{1,8}$), 7.03–7.40 (m, 2, $H_{10,11}$), 7.60–7.90 (m, 2, $H_{9,12}$). Further elution with hexane gave 1,2,3,4-tetrahydrotriphenylene: 202 mg (28%); mp 118–120 °C (lit.[36] 120–121 °C); NMR (CCl_4) δ 1.72–2.17 (m, 4, $H_{2,3}$), 2.80–3.22 (m, 4, $H_{1,4}$), 7.25–7.56 (m, 4, $H_{6,7,10,11}$), 7.66–7.93 (m, 2, $H_{5,12}$), 8.30–8.60 (m, 2, $H_{8,9}$). Finally, elution with benzene gave recovered triphenylene (320 mg, 44%).

(g) 5,6-Dihydrobenz[a]anthracene (PtO_2; 50 psig; 21 h; 315 mg, 1.4 mmol; 50 mg; 20 mL). GLC and NMR analyses showed the product to consist of **2** (20%) and **5** (80%). The latter was collected from the GLC column as a colorless oil: NMR (CCl_4) δ 1.57–1.90 (m, 4, $H_{9,10}$), 2.7 (apparent s, 4, $H_{5,6}$), 2.55–2.98 (m, 4, $H_{8,11}$), 6.77–7.85 (m, 6, aromatic).

Analogous hydrogenation of **2** in the presence of 1% $FeCl_2 \cdot H_2O$ in concentrated HCl gave **5** (85%) and recovered **2** (15%) after only 2.5 h.

(h) 5,6-Dihydro-7,12-dimethylbenz[a]anthracene (PtO_2; 50 psig; 24 h; 720 mg, 2.8 mmol; 100 mg; 10 mL + 10 mL of AcOH). The sole product was 5,6,8,9,10,11-hexahydro-7,12-dimethylbenz[a]anthracene isolated in essentially quantitative yield as an oil: NMR (CCl_4) δ 1.62–1.93 (m, 4, $H_{9,10}$), 2.13 (s, 3, 7-CH_3), 2.39 (s, 3, 12-CH_3), 2.63 (s, 4, $H_{5,6}$), 2.50–2.82 (m, 4 $H_{8,11}$), 6.95–7.50 (m, 4, aromatic).

(i) 4,5-Dihydrobenzo[a]pyrene (PtO_2; 50 psig; 24 h; 340 mg, 1.3 mmol; 45 mg; 10 mL + 10 mL of AcOH). NMR analysis showed the product to consist of 4,5,7,8,9,10-hexahydrobenzo[a]pyrene (25%) and recovered unreacted dihydro compound. Chromatographic separation on a column of 2% TNF on Florisil[15] gave pure 4,5,7,8,9,10-hexahydrobenzo[a]pyrene: mp 87–88 °C; NMR (CCl_4) δ 1.9 (m, 4, $H_{8,9}$), 2.9 (m, 4, $H_{7,10}$), 3.25 (s, 4, $H_{4,5}$), 7.05–8.15 (m, 6, aromatic).

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Registry No. **1**, 56-55-3; **2**, 36914-99-5; **3**, 67064-62-4; **4**, 16434-59-6; **5**, 67064-61-3; **6**, 5981-10-2; **7**, 13090-93-2; **8**, 1610-39-5; **9**, 25486-92-4; benzo[a]pyrene, 50-32-8; 4,5-dihydrobenzo[a]pyrene, 57652-66-1; 3-methylcholanthrene, 56-49-5; 7,12-Me_2BA, 57-97-6; 5,6-H_2-7,12-Me_2BA, 35281-29-9; *cis*-7,12-H_2-7,12-Me_2BA, 24316-23-2; dibenz[a,h]anthracene, 53-70-3; 5,6-dihydrodibenz[a,h]anthracene, 153-34-4; 5,6,12,13-tetrahydrodibenz[a,h]anthracene, 153-31-1; pyrene, 129-00-0; 4,5-dihydropyrene, 6628-98-4; 4,5,9,10-tetrahydropyrene, 781-17-9; phenanthrene, 85-01-8; 9,10-diethylphenanthrene, 15810-14-7; 9,10-diethyl-1,2,3,4-tetrahydrophenanthrene, 73712-68-2; 9,10-diethyl-1,2,3,4,5,6,7,8-octahydrophenanthrene, 73712-69-3; 7,8,9,10-tetrahydrobenzo[a]pyrene, 17750-93-5; 4,5,7,8,9,10,11,12-octahydrobenzo[a]pyrene, 73712-70-6; 4,5,7,8,9,10-hexahydrobenzo[a]pyrene, 73712-75-1; 7,8,9,10,11,12-hexahydrobenzo[a]pyrene, 73712-71-7; 8,9,10,11-H_4-7,12-Me_2BA, 25486-91-3; 5,6,8,9,10,11-H_6-7,12-Me_2BA, 73712-72-8; *trans*-7,12-H_2-7,12-Me_2BA, 23660-33-5; 7-methylbenz[a]anthracene, 2541-69-7; 7-methyl-8,9,10,11-tetrahydrobenz[a]anthracene, 63020-38-2; 12-methylbenz[a]anthracene, 2422-79-9; 12-methyl-8,9,10,11-tetrahydrobenz[a]anthracene, 67099-80-3; 5,6,8,9,10,11-hexahydro-12-methylbenz[a]anthracene, 73712-73-9; 7,12-dihydro-12-methylbenz[a]anthracene, 73712-74-0; dibenz[a,c]-anthracene, 215-58-7; 10,11,12,13-tetrahydrodibenz[a,c]anthracene, 25486-89-9; triphenylene, 217-59-4; 9,10-dihydrophenanthrene, 776-35-2; chrysene, 218-01-9; 5,6-dihydrochrysene, 2091-92-1; 1,2,3,4-tetrahydrochrysene, 2091-90-9.

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Rearrangement of 1-Aryl-2,2-dihalo-1-alkanones[1a]

Norbert De Kimpe,*[1b] Roland Verhé, Laurent De Buyck, and Niceas Schamp

Laboratory of Organic Chemistry, Faculty of Agricultural Sciences, State University of Ghent, Coupure 533, B-9000 Ghent, Belgium

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Reaction of 1-aryl-2,2-dichloro-1-alkanones with alkoxides in the corresponding alcohol afforded a mixture of 1-aryl-2,2-dialkoxy-1-alkanones and 1-aryl-1,1-dialkoxy-2-alkanones. The mechanism was shown to proceed via α-chloro-α′-alkoxy epoxides, which rearranged into 1-alkoxy-1-aryl-1-chloro-2-alkanones, the latter giving the final compounds via either another epoxide intermediate or a solvolysis mechanism. α,α-Dibromo- and α-bromo-α-chloroalkyl aryl ketones behaved analogously, but α-bromo-α-fluoro- and α-chloro-α-fluoroalkyl aryl ketones gave exclusively solvolysis of initially formed 1-alkoxy-1-aryl-1-fluoro-2-alkanones, resulting in rearranged 1-aryl-1,1-dialkoxy-2-alkanones. α,α-Difluoroalkyl aryl ketones did not rearrange but underwent reduction of the carbonyl function on treatment with sodium methoxide in methanol. The influence of varying factors, such as the steric requirements of the alkoxide and the substrate, the concentration of the alkoxide, the aromatic substituent, the temperature, and the halogens, was investigated and correlated to the mechanism involved.

In a preliminary publication we reported on the synthesis of 1-aryl-1,2-alkanediones **4** by reaction of α,α-dichloroalkyl aryl ketones **1** with sodium methoxide in methanol and subsequent acidic hydrolysis of the resulting isomeric α,α-dimethoxy ketones **2** and **3** (Scheme I).[2] α,α-Dichloroalkyl aryl ketones **1** have not received much attention in the literature, but recently an increasing interest revealed several mechanistic and synthetic potentials for this class of compounds.[2-4] α,α-Dichloroaceto-

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