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Hydrogenation of Pyrene and Catalytic Interconversion of Hydropyrenes

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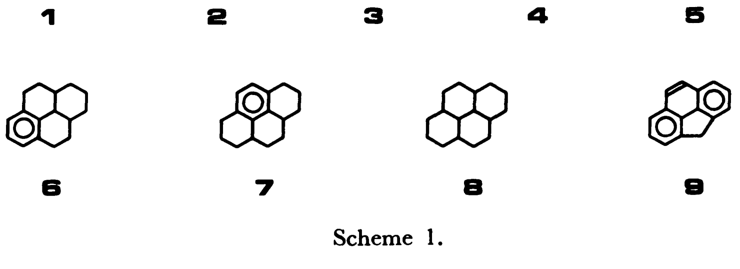
Reexamination on the hydrogenation of pyrene (**1**) with Raney nickel catalyst under atmospheric pressure afforded a mixture of 4,5-di- (**2**), 4,5,9,10-tetra- (**3**), 1,2,3,6,7,8-hexa- (**4**), and 1,2,3,3a,4,5-hexahydropyrene (**5**). The relative amount of each product at the initial reaction stage was determined by time-yield relation of the products. The formation sequence of the products is discussed with reference to the hydrogenations of **2**—**5**: **4** may be formed independent of **2**, and **2** is converted to **3**. Hydropyrene **5** may be produced from **1** mainly through the same σ-adsorbed species which also leads to **2**. The hydrogenation of **1** with palladium and platinum catalysts gave similar results as with nickel. With nickel and palladium catalysts the hydrogenation of **1** was faster than that of 4*H*-cyclopenta[*def*]phenanthrene (**9**). However, with platinum the hydrogenation of **1** was slower than that of **9**. Catalytic interconversion of **2**—**5** was examined at 240 °C under an argon pressure of 90 kg cm^{-2}. Hydroarene **2** was easily dehydrogenated, and **3** and **5** were interconverted to a fair extent. Therefore, **2**, **3**, and **5** may be good hydrogen donor solvents for coal liquefaction.

The catalytic hydrogenation of polycyclic aromatic hydrocarbons (PAHs) has been investigated extensively from both stereochemical and mechanistic standpoints.[1,2] The products are of interest both as synthetic intermediates,[1] and because of their carcinogenic properties.[1,3,4] In addition, partially hydrogenated PAHs have recently been used as hydrogen donor solvents in coal liquefaction.[5] For our continuing study of PAHs having active methylene such as fluorene,[6] we have compared the reactivity of hydrogenation of PAHs possessing active methylene with that of PAHs possessing no active methylene such as pyrene (**1**). The hydrogenation of **1** is of interest in particular from the following three viewpoints. One of those is the hydrogenation sequence. It has been known that the hydrogenation of **1** gives 4,5-di- (**2**),[7] 4,5,9,10-tetra- (**3**),[8] 1,2,3,6,7,8-hexa- (**4**),[9] 1,2,3,3a,4,5-hexa- (**5**),[9] isomeric deca- (**6**, **7**),[10] and perhydropyrenes (**8**)[11] under various reaction conditions (Scheme 1).[12] Although the previous papers have studied the function of temperature and pressure in addition to catalysts, the hydrogenation sequence was not so clear.[10] This is because the change of the yield of each product has not yet been examined as a function of reaction time. The study of the hydrogenation of **1** with respect to the reaction time may shed light on the reaction pathway and be useful to uncover the reaction conditions to obtain specific hydroarenes.

A second consideration is the relative reactivity of **1** among PAHs. For example, the rate of hydrogenation of **1** to **2** with palladium-on-carbon catalyst has been reported to be comparable to the rate of the hydrogenation at the 8,9-double bond of 4*H*-cyclopenta[*def*]phenanthrene (**9**).[13] We have recognized in the study of the hydrogenation of **9**[14] that the reduction of **1** is slower than that of **9** when platinum oxide is used as catalyst. The abnormality of palladium as a catalyst in the platinum group metals has been pointed out in the hydrogenation of aromatic compounds[15,16] and cycloolefins.[17] The abnormality may be caused by the fact that palladium in particular adsorbs reactants very weakly[18] and the rate- and product-controlling steps of hydrogenation with palladium may differ from that of hydrogenation with platinum.[19]

The third interest concerns the ability of **2**—**5** as hydrogen donor solvents in coal liquefaction. Mochida *et al.* have reported the effectiveness of hydrogenated pyrene mixture as the solvent.[20] The direct coal liquefaction occurs mainly by radical hydrogen transfer, and hence, the ability of hydrogen transfer of the solvent may play an important role in the coal liquefaction process. The hydrogen donat-



Scheme 1.

ing property of partially hydrogenated aromatics has been determined by disproportionation of the substrate or by the reaction of substrate with hydrogen acceptor as the cases of cyclohexene,[21] naphthalene,[22] phenanthrene,[23] and anthracene[12] derivatives. With regard to the partially hydrogenated pyrenes, no reports describing such reactions are limited to a few examples.[24]

The present paper deals with the hydrogenation of **1** under mild conditions to indicate the reaction pathway of **1**. Also, it examines the competitive hydrogenation of **1** and **9**. Finally, it considers the catalytic interconversion of hydropyrenes, **2**—**5** to clarify the ability of these compounds as hydrogen donors.

Results and Discussion

Hydrogenation of **1** in the presence of Raney nickel (W-7) was carried out in ethanol at room temperature under atmospheric pressure of hydrogen to afford **2**, **3**, **4**, and **5** as illustrated in Fig. 1. In addition, more highly hydrogenated arenes, **6**—**8**, were detected in small amounts, but they were not further studied. Also, the hydrogenations of **2**—**5** were examined under similar conditions. The relative amount of each product at the initial reaction stage was determined by a known procedure[15,25] (Table 1). The rate constant of the conversion of each substrate was roughly estimated from time-conversion relation, based on the assumption that the reaction followed zero-order kinetics in reactant till its complete conversion.

The results suggest that **2** and **4** are mainly formed from **1**, and the main portion of **2** is converted gradually into **3**. Hydroarene **4** is formed independent of the formation of **2**. The interconversion of hydropyrenes except **3** may be negligible under these conditions as is explained later. Therefore, the adsorption of the planar molecule **1** onto the catalyst surface (A) could take place in two different manners; namely at the C_4-C_5 bond (B) and at the biphenyl ring system (C)[26] (Scheme 2). Either the half-hydrogenated state (D) at the C_4 atom may undergo desorption to give **2**, or may be converted to the adsorption state (E)[19] at the biphenyl ring moiety to afford **5** by subsequent hydrogenation. In a similar manner, **2** can give **3** *via* (F) and **3** may be hydrogenated slowly to **4** and **5** through hydrogen transfer. Absorbate (C) may yield **4** and **5** *via* (G) and (H), respectively. The process to **5** through (H) may be a minor route in the hydrogenation of **1** because **5** is thermodynamically less stable than **4** as is explained later.[26]

The hydrogenation of **1** was also carried out in

Table 1. Relative amount of **2**—**7** formed in the hydrogenation of pyrene and hydropyrenes with Raney nickel at initial stage

Reactant	Relative amount/mol%				Rate constant
	2	**3**	**4**	**5**	mol s^{-1} g-cat.$^{-1}$
1	39	6	37	12	2.3×10^{-7}
2		78	7	6	9.3×10^{-8}
3			58	32	2.2×10^{-9}
4	90(for **7**)				5.4×10^{-10}
5	53(for **7**)		44(for **6**)		2.0×10^{-9}
1[a)]	64	6	19	11	
1[b)]	32	18	14	8	

a) With Pd-C. b) With PtO_2.

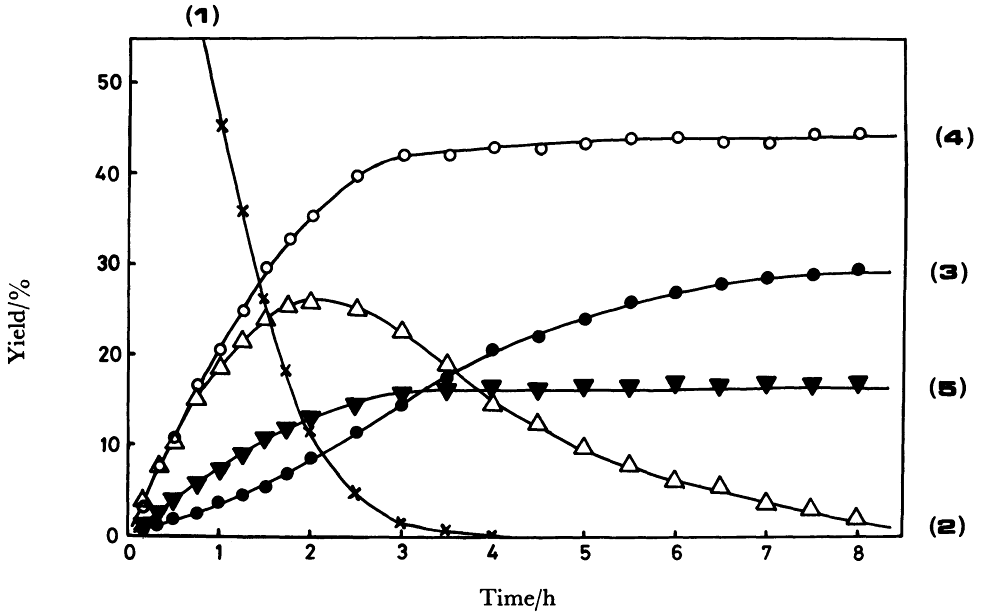
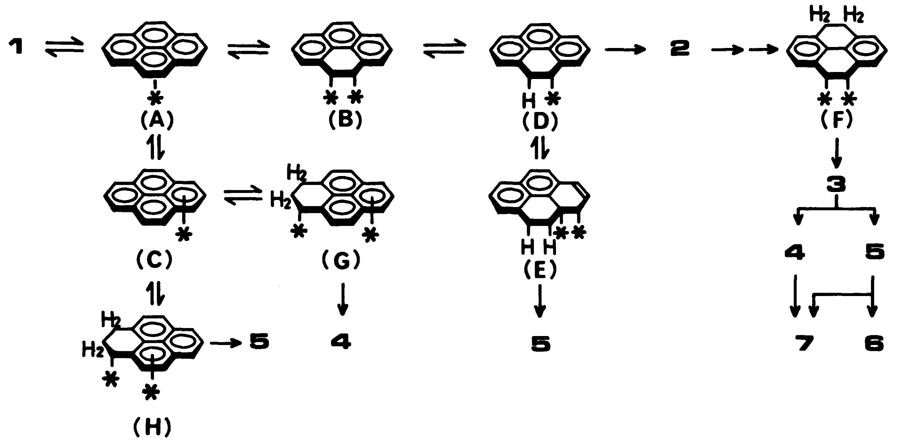


Fig. 1. Figure 1. The process of hydrogenation of **1**.
—✕— (**1**); —△— (**2**); —●— (**3**); —○— (**4**); —▼— (**5**).



Scheme 2. The presumptive sequence of hydrogenation of **1**. (The asterisk shows the active surface of catalyst.)

TABLE 2. HYDROGENATION OF **1** WITH SOME CATALYSTS

Catalyst	Product distribution/%					$k(\mathbf{1})/k(\mathbf{9})$[a]
	1	**2**	**3**	**4**	**5**	
R-Ni(W-7)	45	19	4	21	7	1.37
Pd-C(10%)	46	33	4	11	5	1.74
PtO_2	50	22	5	6	3	0.75
Mo-Co	47	11	3	24	14	

a) Relative conversion of **1** and **9**.

the presence of palladium-on-carbon or platinum catalyst at 50 °C under a hydrogen pressure of 5 kg cm^{-2} (1 kg cm^{-2}=98066.5 N m^{-2}) to afford **2**—**8**. Table 2 shows the product distribution at about 50% conversion of **1**. The distribution with Mo–Co catalyst was estimated by comparison of the NMR data described elsewhere[27] with the NMR spectra of an authentic mixture of pure **1**—**5**. Since the overall trend of the yield is similar to the case of Raney nickel, the reaction sequence in the presence of palladium or platinum catalyst may be explained as in the case of the nickel catalyst. The palladium catalyst in particular gives **2** in relatively high yield (Table 1). On the contrary, significant amounts of **6**—**8** are formed with the platinum catalyst in analogy with the example of **9**.[14]

The relative reactivity of **1** and **9** was examined by a competitive method. The hydrogen pressure was maintained as constant as possible during the reaction in order to remove the factor of hydrogen pressure.[16,28,29] The reactions followed zero-order kinetics in reactants till about half-conversion of reactants. Table 2 shows that **1** is more reactive than **9** over the nickel and palladium catalysts, in contrast to hydrogenation using platinum.

The ratio of conversion of **1** and **9** may be regarded as the overall results of two factors. One is the adsorption equilibrium of each reactant and the other is the rate factor of each adsorbed species. If the adsorbed species of one reactant disturbs the adsorption of the other reactant, the rate of the latter reactant estimated by the competitive method may be less than that determined independently. Therefore, the ratio of conversion in Table 2 may differ from that obtained independent hydrogenations of **1** and **9**. Nevertheless, the difference of the ratio due to the catalyst is thought in some degree to indicate the difference of reactivities of each component. The real reason could be complex, but **9** is presumed to be more reactive than **1**, because **9** is strained owing to the five-membered ring. In fact, **9** is known to give an 8,9-dihydro derivative by treatment with sodium in ethanol[13] and to give 8,9-dibromide by the action of bromine.[30]

TABLE 3. CATALYTIC INTERCONVERSION OF HYDROPYRENES[a]

Reactant	Product distribution/%				
	1	**2**	**3**	**4**	**5**
1	99	1			
2	70	25	2	2	1
3	48	18	4	20	8
3[b]	97	3	*	*	*
3[c]	*	1	99	*	*
4	20	9	1	58	9
5	19	7	1	21	48

a) Reaction was carried out with platinum at 240 °C under an argon pressure of 90 kg cm^{-2} for 10 h. The asterisk shows that trace amount (<0.4%) was detected by GLPC. b) 240 °C, 9 kg cm^{-2}, 3 h. c) 50 °C, 90 kg cm^{-2}, 50 h.

Catalytic interconversion of hydropyrenes, **2**—**5**, was examined at 240°C under an argon pressure of 90 kg cm^{-2} with platinum catalyst (Table 3). Dehydrogenation takes place due to increase of the resonance stability by aromatization. Easily dehydrogenated reactants such as **2** or **3** may be good hydrogen donors. The thermodynamical stability of **4** compared with that of **5** would be supported by the fact that **4** was easily formed from **5**, as contrasted with the yield of **5** from **4**. Consequently, the interconversions of **3** and **5** occur easily. This is the reason why **2**, **3**, and **5** may be good hydrogen donors for coal liquefaction solvent.

Experimental

All melting points are uncorrected. The ^{1}H NMR (in CCl$_4$), IR (KBr-disk), UV (in cyclohexane), and mass spectra were recorded using the same apparatus as described elsewhere.[14]

The distribution of products was examined by GLPC with a GC-8A gas chromatograph (Shimadzu) equipped with a column (3 mmϕ, 1 m) containing Dexsil 300GC (5%) on Chromosorb WAW (80—100 mesh) at 195 °C under 1 kg cm^{-2} of nitrogen. Each peak area of **1** (retention time; 9.5 min), **2** (7.2 min), **3** (4.6 min), **4** (6.3 min), **5** (5.8 min), **6** (3.4 min), and **7** (3.8 min) was compared using TR-2217 integrator (Takeda Riken). The competitive hydrogenation of **1** and **9** was also examined by the same gas chromatograph containing Silicone OV-17 (5%) as liquid phase at 165 °C. Each peak area of **1** (8.8 min) and **9** (3.8 min) was compared with that of tetracosane (13.5 min) as an internal reference.

The catalysts used in this experiment were the same as those described elsewhere.[14]

Hydrogenation of 1 over Palladium-on-Carbon. 400-mg of Pd–C (10%) suspended in AcOEt (5 ml) was pretreated at 50±1 °C under hydrogen pressure of 5 kg cm^{-2} for 1 h. A solution of **1** (202 mg, 1 mmol) in AcOEt (25 ml) was added to the suspension. After 4 purges with hydrogen, the mixture was stirred at 50 °C and 5 kg cm^{-2}. A small amount (*ca.* 0.2 ml) of the mixture was taken out, filtered, and submitted to GLPC after 30 min, 1 h, and additionally every 1 h.

After 7 h, the test portion showed the proportion to be **1** (46%), **2** (33%), **3** (4%), **4** (11%), **5** (5%), and others (1%). All the mixtures were filtered and evaporated to dryness, and the residues chromatographed on an alumina column (200 g, 16 mmϕ, 120 cm) with hexane. The rate of effusion was 1.2 min ml^{-1}, and the eluate was collected as 10-ml units. Fraction from 840 to 1140 ml gave 21.4 mg (10%) of **4**: mp 131—132 °C (from hexane) (lit,[9] mp 132—134 °C); NMR, δ=1.99 (4H, q, J=6.5 Hz), 3.02 (8H, t), and 6.95 (4H, s); UV, $\lambda_{\max}$ 235 (log ε 4.81), 286 (3.87), 309 (4.15), 315 (3.71), 323 (3.32), and 330 nm (3.49). Fraction between 1240 and 1490 ml afforded 5.8 mg (3%) of **3**: mp 135—137 °C (hexane) (lit,[8] mp 135—136 °C); NMR,[26] δ=2.85 (8H, s) and 6.96 (6H, s); UV, $\lambda_{\max}$ 215 (log ε 4.59), 270 (4.18), and 280 nm (4.27). Fraction at 1490—2050 ml gave 11.0 mg (5%) of **5**: mp 104—106 °C (hexane) (lit,[9] mp 105 °C); NMR, δ=1.25—3.26 (11H, m) and 6.89—7.46 (5H, m); UV, $\lambda_{\max}$ 227 (log ε 4.78), 233 (4.93), 285 (3.80), 294 (3.70), 311 (3.17), and 325 nm (3.21). Fraction between 2130 and 3640 ml afforded 52.6 mg (26%) of **2**: mp 131—132 °C (hexane) (lit,[7] mp 132 °C); NMR,[26] δ=3.24 (4H, s) and 7.23—7.67 (8H, m); UV,[7] $\lambda_{\max}$ 217 (log ε 4.63), 260 (4.67), 282 (4.17), 287 (4.13), 299 (4.00), 319 (3.03), and 335 nm (3.19). Fraction at 3830—4440 ml gave 90.0 mg (45%) of **1**, mp 149 °C.

In addition, fraction ranging from 540 to 840 ml afforded an oil (9.9 mg) which was determined as a mixture of **4**, **6**, **7**, and **8** by means of GC–MS.

Hydrogenation of 1 over Platinum. A 50.2-mg portion of platinum oxide in AcOEt (5 ml) was treated with hydrogen for 1 h at 5 kg cm^{-2}. A solution of **1** (101 mg, 0.5 mmol) in AcOEt (20 ml) was added to the vessel and the mixture was stirred at 50 °C under hydrogen pressure of 5 kg cm^{-2}.

Hydrogenation of 1 over Raney Nickel. A mixture of **1** (202 mg, 1 mmol) in HOEt (40 ml) was shaken with Raney nickel catalyst (W-7, 0.4 g as alloy) at room temperature under hydrogen at atmospheric pressure. The composition of the mixture was determined by GLPC as is shown in Fig. 1.

Hydrogenation of 2. Compound **2** (40.8 mg, 0.2 mmol) in HOEt (15 ml) was shaken with Raney nickel (W-7, 0.2 g) in a similar manner to **1**. The distribution of the test portion was **2** (trace), **3** (76%), **4** (9%), and **5** (6%) after 3 h and was **3** (74%), **4** (11%), and **5** (6%) after 10 h.

Hydrogenation of 3. A solution of **3** (41.2 mg, 0.2 mmol) in HOEt (15 ml) was allowed to react in the presence of Raney nickel (W-7, 0.75 g). The test portion showed the proportion to be a mixture of **3** (86%), **4** (8%), **5** (4%), **6** (1%), and **7** (1%) after 3 h and to be **3** (42%), **4** (33%), **5** (trace), **6** (7%), and **7** (11%) after 23 h.

Hydrogenation of 4. A mixture of **4** (41.6 mg, 0.2 mmol) in HOEt (15 ml) was treated with Raney nickel (W-7, 1 g) in a similar manner to **1**. The distribution of the mixture was as follows: **4** (89%), **6** (1%), and **7** (7%) after 3 h and **4** (62%), **6** (2%), and **7** (32%) after 27 h.

Hydrogenation of 5. Compound **5** (41.6 mg, 0.2 mmol) in HOEt (15 ml) was shaken with Raney nickel (W-7, 1 g) as above. The proportion of the mixture was **5** (72%), **6** (12%), and **7** (15%) after 3 h and **5** (5%), **6** (40%), and **7** (49%) after 19 h.

Competitive Hydrogenation of 1 and 9. Over Raney Nickel. A mixture of **1** (51.1 mg, 0.26 mmol), **9** (45.1 mg, 0.24 mmol), and tetracosane (31.0 mg) in HOEt (30 ml) was shaken with Raney nickel (W-7, 0.6 g) at room temperature under hydrogen at atmospheric pressure. Every 15 min, a small portion was taken out and submitted to GLPC.

Over Palladium-on-Carbon. A mixture of **1** (50.5 mg, 0.25 mmol), **9** (50.3 mg, 0.27 mmol), tetracosane (35.5 mg), and Pd–C catalyst (10%, 600 mg, pretreated with hydrogen at 50 °C under 5 kg cm^{-2} for 1 h) in EtOAc (30 ml) was stirred at 50 °C and 5 kg cm^{-2} of hydrogen.

Over Platinum Catalyst. Platinum oxide (50.1 mg) in AcOEt (5 ml) was pretreated with hydrogen at 50 °C for 1 h under 5 kg cm^{-2}. A mixture of **1** (50.8 mg, 0.25 mmol), **9** (47.5 mg, 0.25 mmol), and tetracosane (34.5 mg) in AcOEt (25 ml) was poured into the solution, and all was stirred at 50 °C under a hydrogen atmosphere of 5 kg cm^{-2}.

Catalytic Interconversion of Hydropyrenes. General Procedure. About 1-mg portion of platinum oxide (1.0—1.5 mg) was placed in a tube (0.5 mmϕ, 6 cm), cyclohexane (0.1 ml) was added, and it was stirred at 50 °C under 5 kg cm^{-2} of hydrogen pressure for 1 h. Reactant (0.05 mmol per 1 mg of PtO$_2$) was added with cyclohexane (0.4 ml). After purge by argon, the top of the tube was extended to 12 cm in length with a diameter of *ca.* 0.1 mm. The reaction tube was placed in an autoclave which contained hexane

(20 ml), and it was maintained at 240—250 °C under an argon pressure of 85—95 kg cm^{-2} during 10 h. Upon cooling the mixture, the content was submitted to GLPC. A part (<3%) of the reaction mixture flowed out into outer hexane; the proportion of the hexane solution was similar to that of the reaction mixture.

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