March, 1984] Bull. Chem. Soc. Jpn., 57, 725—728 (1984)

Catalytic Reduction of 4*H*-Cyclopenta[*def*]phenanthrene under Mild Conditions

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(Received April 22, 1983)

The catalytic hydrogenation of 4*H*-cyclopenta[*def*]phenanthrene over Raney nickel afforded 8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene and 1,2,3,3a-tetrahydro derivative. Under these conditions, di- and tetrahydro compounds were reduced into two diastereomers, *cis*-3a-*cis*-9a- and *trans*-3a-*cis*-9a-1,2,3,3a,8,9,9a,9b-octahydro-4*H*-cyclopenta[*def*]phenanthrene. The reduction over palladium gave a dihydro compound and a platinum catalyst provided products analogous with those obtained over Raney nickel.

One of polynuclear aromatic hydrocarbons, 4*H*-cyclopenta[*def*]phenanthrene (**1**), is made up of one five-membered and three six-membered rings, and is of interest for its the carcinogenic property.[1] The reactivity of **1** with electrophiles has been found to differ from those of phenanthrene, fluorene, and pyrene.[2] The C_8–C_9 bond of **1** shows the double bond character. For example, **1** was converted into the stable C_8–C_9 ozonide[3] and into the 8,9-diketone.[4,5]

Catalytic hydrogenation of **1** has been reported to give only 8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene (**2**) when it is carried out using copper chromite at 160 °C[6] or over palladium-on-charcoal at room temperature.[7] The reactivity of C_8–C_9 bond of **1** would seem to be preferable to that of C_9–C_{10} bond of phenanthrene, and may be ascribed to the distorted phenanthrene moiety of **1** by the central methylene bridge.

Our present interest is whether the hydrogenation of **1** proceeds regiospecifically. For example, reduction of benz[*a*]anthracene using a Pd/C catalyst took place at the K-region to give 5,6-dihydro compound in a predominant yield, while an analogous reaction in the presence of a Pt catalyst occurred regiospecifically to afford 8,9,10,11-tetrahydro compound.[8]

The present paper deals with the detailed investigation on the catalytic reduction of **1** in order to clarify the reactivity of **1** and the related derivatives. This may give information on the hydrogenation of other aromatic hydrocarbons.

Results and Discussion

The catalytic hydrogenation of **1** was carried out at room temperature under an atmospheric pressure of

Table 1. Catalytic hydrogenation of 4*H*-cyclopenta[*def*]phenanthrenes

Reactant	Catalyst (m/g)	Time/h	Proportions/%					
			1	**2**	**3**	**4a**	**4b**	**5**
1	R-Ni(W-7) (2.0)	1/2	Trace	72	2	12	14	0
		7	0	Trace	0	43	57	0
1	R-Ni(W-7) (1.0)	3/4	8	73	3	7	9	0
2	R-Ni(W-7) (2.0)	1/2		78		8	14	0
		8		Trace		36	64	0
3	R-Ni(W-7) (1.0)	1/2			20	46	34	0
		1			0	55	45	0
1	R-Ni(W-4) (2.0)	1/3	0	82	Trace	8	10	0
		6	0	0	0	41	59	0
		21	0	0	0	33	54	13
1	Pd/C(5%) (2.0)	1	71	25	<1	<1	4	0
		24	<1	92	Trace	2	6	0
1	PtO_2(0.05)	1/2	76	5	1	5	6	7
		7	15	21	Trace	24	30	11
		24	0	0	0	11	47	42
1[a]	PtO_2(0.05)	1	46	15	<1	12	18	8
		3	13	20	Trace	24	31	12
2	PtO_2(0.05)	1/2		72		5	15	8
		7		Trace		5	69	26
3	PtO_2(0.024)	1/2			79	13	8	0
		5			0	55	32	13

a) Under a pressure of 5 kg cm^{-2}.

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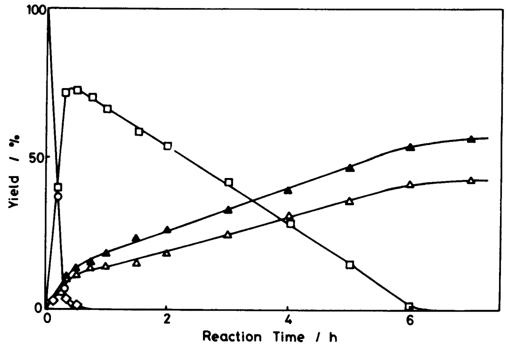
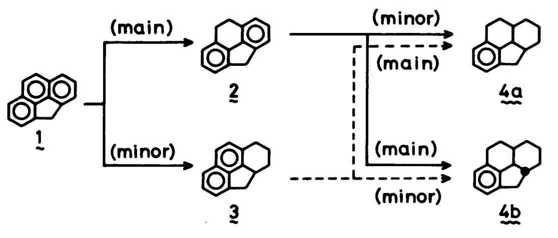


Fig. 1. Typical process of hydrogenation of **1** over R–Ni (**1**, 1 mmol; R–Ni, W-7, 2.0 g).
—○—: **1**, —□—: **2**, —◇—: **3**, —△—: **4a**, —▲—: **4b**.



Scheme 1. Diagram of hydrogenation of **1**.

hydrogen, as is summarized in Table 1. These conditions are controllable and practical for preparation of hydroarenes.

Figure 1 shows a typical process of the reaction of **1** using a Raney nickel catalyst (W-7). The hydrocarbon **1** was easily converted into **2** (max. yield 75%) and 1,2,3,3a-tetrahydro-4*H*-cyclopenta[*def*]phenanthrene (**3**)[9] (max. yield 5%) in an earlier stage. Dihydro compound **2** was gradually hydrogenated under these conditions to afford two diastereomeric 1,2,3,3a,8,9,9a,9b-octahydro-4*H*-cyclopenta[*def*]phenanthrenes having melting points of 53—55 °C (**4a**) and of 63—65 °C (**4b**). On the other hand, tetrahydro compound **3** was smoothly reduced into **4a** and **4b**. Further hydrogenations of **4a** and **4b** to perhydro derivatives (**5**)[10] did not proceed under the same conditions. The amount of catalyst affected only the progress of hydrogenation, but not the proportion of the products in the range of 0.2 g to 2.0 g of catalyst per 1 mmol of **1**.

The hydrogenation of **1** over a neutral nickel catalyst (W-4) afforded, **2**, **3**, **4a**, and **4b**, similar to the case of W-7. Minor but significant differences due to the catalytic species could be detected: one of these is that the reaction was accelerated by W-4 catalyst. Second, about 13% of **5** was formed after 21 h, different from the instance of W-7.

Hydrogenation of **1** over a palladium-on-charcoal (5%) was substantially slow and furnished predominantly **2**. Reduction of **2** was scarcely possible, since more than 88% of **2** remained intact after a period of 48 h.

Figure 2 shows a typical pattern of the hydrogenation of **1** in the presence of a platinum oxide catalyst. Arene **1** was reduced to **2** and **3**, as was the case over Raney nickel, but those di- and tetrahydroarenes were again converted into **4a** and **4b**. Hydrogenation of **4a** was faster than that of **4b** under these conditions.

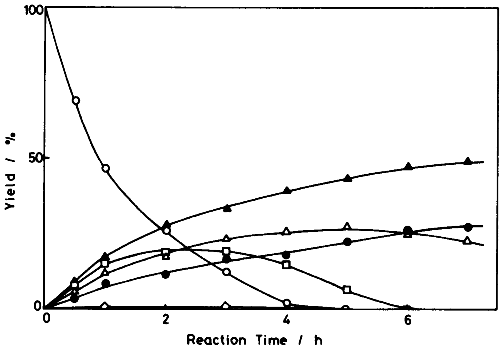


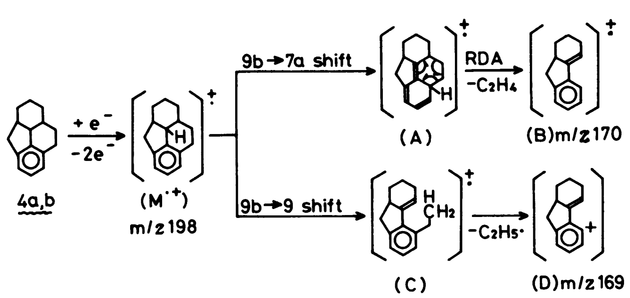
Fig. 2. Typical process of hydrogenation of **1** over PtO_2 (**1**, 1 mmol; PtO_2, 50 mg; 5 kg cm^{-2}).
—○—: **1**, —□—: **2**, —◇—: **3**, —△—: **4a**, —▲—: **4b**, —●—: **5**.

Four kinds of diastereomers in 1,2,3,3a,8,9,9a,9b-octahydro derivatives of **1** may exist, namely (i) *cis*-3a-*cis*-9a, (ii) *trans*-3a-*cis*-9a, (iii) *trans*-3a-*trans*-9a, and (iv) *cis*-3a-*trans*-9a. However, the former two structures are possible and the latter two are impossible, judging from the consideration that the catalytic hydrogenation would proceed *via* cis-addition and that **3** gave both **4a** and **4b**. The first suggestion on the assignment is ascribed to the findings that the non-planar **3** afforded **4a** more predominantly than **4b** over a nickel catalyst, due to the catalytic hindrance. One of the diastereomers, **4a** may be assigned to be *cis*-3a-*cis*-9a. Isomeric **4b** (*trans*-3a-*cis*-9a), whose protons at both 9a- and 9b-positions are located *trans* with respect to 3a-hydrogen, would thermodynamically be more stable than **4a**. The boiling point of **4a** seems to be higher than that of **4b**, based on the GLPC using a nonpolar liquid phase.

The yield of **4b** is more than that of **4a** in reduction of the planar molecule **2**. This would seem to disagree with the general finding that the hydrogenation of aromatics is controlled kinetically to afford all-*cis* compound under the conditions of relatively low temperature using nickel or platinum catalyst. The internal strain of **4a** may be significant due to the *cis-cis* configuration of the *peri*-condensed skeleton, differing from the case of hydrogenated phenanthrene. Consequently, the hydrogenation of **2** could be controlled thermodynamically.

In an earlier stage of the reduction of **3** using a platinum oxide, the ratio of **4a**/(**4a**+**4b**) is larger than the case over a nickel catalyst; this accords with the von Auwers-Skita rule. The decrease of the ratio, **4a**/(**4a**+**4b**), with the extension of the reaction time would be ascribed to the fact that unstable **4a** rather than stable **4b** is easily reduced to perhydro compound 5.

The relative intensity of the molecular ion to the total ion intensity of **4b** is greater than the case of **4a**. This is consistent with the assignment of **4a** and **4b**, since M$^{\cdot+}$ of *trans*- or *exo*-form isomer is generally more intense than that of *cis*- or *endo*-isomer.[11] The fragmentations of **4a** and **4b** show remarkable differences. The relative intensities at *m/z* 170 and *m/z* 169 are 62 and 80% for **4a** and 88 and 8% for **4b** to each



Scheme 2. Speculation on fragmentation pathways of **4a** and **4b**.

molecular ion intensity.

The ion (B) at *m/z* 170 is speculated to form through the 1,3-hydrogen shift of H_{9b} of $M^{\cdot+}$ to C_{7a} to give ion (A), followed by retro-Diels-Alder reaction (RDA) with *cis*-elimination of ethylene under the electron-impact conditions, as is shown in Scheme 2. The generation of ion (D) at *m/z* 169 is considered to be mainly due to the 1,3-hydrogen shift of H_{9b} to C_9 to yield ion (C) and the elimination of ethyl radical from (C). Ions (B) plus (D) from **4a** (1.4 times of $M^{\cdot+}$) are more intense than those from **4b**; this would be due to the stabilities of **4a** and **4b** under the conditions used.[11,12] Isomer **4a** may be less stable thermodynamically than **4b** due to the distorted configuration, and readily undergoes dissociation to ions (A) and (C).

The migration of hydrogen during the hydrogenation is interesting. 9,10-Dihydrophenanthrene has been found to be converted to phenanthrene and tetrahydrophenanthrene under vigorous conditions (100—140 atom, 250 °C).[13] The conversion of **2** to **3** is neglected because that no **3** was detected in the reduction of **2** in all cases examined here. This suggests that **2** and **3** are independently formed by different attacks on the 8,9-positions and on the 1,2,3,3a-positions, respectively. Preferential formation of **2** may be due to the high double bond character at the C_8–C_9 bond.

In the catalytic reduction of **1** under mild conditions, the palladium catalyst seems useful for the preparation of **2**: this accords with the suggestion by Fu, Lee, and Harvey.[8] Raney nickel is available for the synthesis of octahydro compounds **4a** and **4b**, and a platinum catalyst affords further hydrogenated arenes such as **5**. The order of reactivity agrees only with that of the activity of catalyst (Pt>Ni>Pd) used as evaporated metallic films on deuteration of benzene.[14]

Experimental

All the melting points are uncorrected. The ^{1}H NMR, ^{13}C NMR, IR, and UV data were recorded on a JNM-C-60HL (JEOL, 60 MHz, using Me_4Si in $CDCl_3$), a JNM-FX-100 (JEOL, 25 MHz, from Me_4Si in $CDCl_3$), an IR-G (JASCO, as KBr-disk), and a UV-180 (Shimadzu, in cyclohexane) spectrometers, respectively. The mass spectra were measured (direct inlet) at 70 eV on an M-80 GC-MS apparatus (Hitachi) with an M-003 computer data system. An equimolar mixture of **4a** and **4b** was submitted to GC-MS (column: Silicone OV-1, 10%, 1 m, 160 °C) at 20 eV to compare the relative intensities of $M^{\cdot+}$; 32.1% of $\sum_{18}$ in **4a** and 35.7% of $\sum_{18}$ in **4b** were observed.

The GLPC data were obtained with a JGC-1100FP gaschromatograph (JEOL) equipped with a column (3 mmϕ, 0.2 m) containing PEGA (10%) on Diasolid (80—100 mesh) at 145 °C under 0.59 kg cm^{-2} of nitrogen, by means of comparison of each peak area using a TR-2217 automatic integrator (Takeda Riken).

The Raney nickel catalysts (W-4 and W-7) were prepared by standard procedure using nickel–aluminium alloy (48% of nickel): the quantity of catalyst was indicated as weight of the alloy. The palladium-on-charcoal (5%) was also prepared by a known method. The Adams platinum oxide was purchased from Kawaken Fine Chemical Co.

In Table 1, the amount of catalyst means the weight based on 1 mmol of reactant in HOEt (50 ml) over nickel catalyst or in EtOAc (50 ml) over Pd–C or PtO_2. Docosane was added as an internal reference for quantitative treatment.

Hydrogenation of 1 over R-Ni (W-7). To a mixture of **1** (190 mg, 1 mmol) in HOEt (30 ml) placed in the Paal-type hydrogenation flask (so-called "Magen"), R-Ni catalyst was added to HOEt (20 ml) (time, 0 h). Upon substitution of air with hydrogen (4 times), the flask was shaken at room temperature under an atmosphere of hydrogen. In order to follow the sequence of reduction, a small amount of reaction mixture (*ca.* 0.2 ml) was taken out *via* Teflon septum by an injector, filtered and submitted to GLPC after each 1/6, 1/3, 1/2, 3/4, 1, 3/2, 2 h and additionally every 1 h.

Hydrogenation of 1 over Adams PtO_2. Platinum oxide (25.4 mg) was added with 10 ml of EtOAc into a solution of **1** (95.1 mg, 0.5 mmol) in EtOAc (15 ml) placed in a stainless steel autoclave. After 4 purges with hydrogen, the mixture was stirred at room temperature under a hydrogen pressure of 5.0 kg cm^{-2}. After each prescribed time, the proportion of mixture was measured by GLPC.

Hydrogenation of 3 over R-Ni (W-7). Tetrahydro compound **3** (97.1 mg, 0.5 mmol) was treated with R-Ni (W-7, 0.5 g) in HOEt (25 ml) for 2 h. The reaction mixture was filtered and the residue was extracted with HOEt (100 ml). The filtrate and extract were combined and evaporated to dryness. The residue was extracted with cyclohexane (10 ml), and the solution was chromatographed on a column (17 mmϕ; 85 cm) of silica gel with petroleum ether (bp 50—65 °C) as eluent. The rate of effusion was *ca.* 0.65 ml/min. The eluate, which ranged from 287 ml to 333 ml, gave 39.2 mg (40%) of **4b**, mp 63—65 °C, by recrystallization from petroleum ether: retention time, 12.8 min (on a GLPC with a column containing Silicone SE-30, 120 °C). IR: 3050, 2970, 2880, 1604, 1482, 1443, 1329, 1152, 1083, 944, 842, 807, and 762 cm^{-1}. UV_{max}: 220 (log ε 3.91), 268 (2.86), and 276 nm (2.86). ^{1}H NMR: δ=0.73—3.14 (m, 15H) and 6.80—7.05 (m, 3H). ^{13}C NMR: δ=22.8, 24.6, 25.1, 27.3, 28.6, 32.4, 38.9, 41.0, 44.2, 122.4, 124.8, 126.2, 133.9, 141.3, and 142.9. MS *m/z* ($\sum_1$): 199 (4.2), 198 (25.9, $M^{\cdot+}$), 197 (7.6, $M^{\cdot+}-1$), 171 (3.3), 170 (22.9, $C_{13}H_{14}$), 169 (2.1, $C_{13}H_{13}$), 156 (1.4, $C_{12}H_{12}$), 155 (3.6, $C_{12}H_{11}$), 142 (5.0, $C_{11}H_{10}$), 129 (3.5, $C_{10}H_9$), 128 (1.2, $C_{10}H_8$), and 28 (0.5, C_2H_4). Found: C, 90.67; H, 9.08%. Calcd for $C_{15}H_{18}$: C, 90.85; H, 9.15%.

The fraction from 333 ml to 352 ml was a mixture (17.6 mg) of **4a** and **4b**.

In addition, 36.4 mg (37%) of **4a**, mp 53—55 °C (from hexane), was afforded from the eluate, which ranged from 352 ml to 404 ml: retention time, 16.8 min (SE-30, 120 °C). IR: 3050, 2970, 2870, 1603, 1492, 1450, 1332, 843, and 787 cm^{-1}. UV_{max}: 212 (log ε 4.14) and 266 nm (2.69). ^{1}H NMR: δ=0.77—3.05 (m, 15H) and 6.82 (3H, s). ^{13}C NMR: δ= 24.0, 26.1, 29.2, 41.4, 44.4, 125.9, 131.1, and 144.3. MS *m/z* ($\sum_1$): 199 (4.2), 198 (25.1, $M^{\cdot+}$), 197 (2.1, $M^{\cdot+}-1$), 171 (2.1), 170 (15.6, $C_{13}H_{14}$), 169 (20.0, $C_{13}H_{13}$), 156 (7.8, $C_{12}H_{12}$), 155 (4.9, $C_{12}H_{11}$), 142 (3.7, $C_{11}H_{10}$), 129 (1.0, $C_{10}H_9$), 128 (0.6, $C_{10}H_8$), and 28 (0.5, C_2H_4). Found: C, 90.92; H, 9.32%. Calcd for $C_{15}H_{18}$: C, 90.85; H, 9.15%.

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