A Novel Approach to Extended Phenalenones

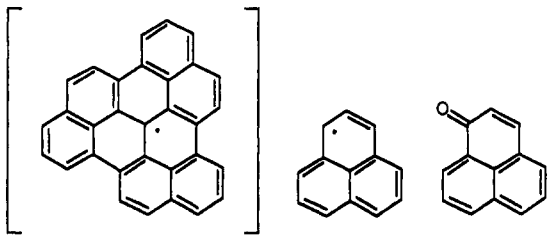
Masahiko Suenaga,* Yuji Miyahara, and Takahiko Inazu

Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki 6-10-1, Higashi-ku, Fukuoka 812, Japan

Received May 18, 1993

Introduction

While extensive experimental and theoretical studies[1,2] on phenalenyl **2** and its derivatives have been made in comparatively small π-systems, the properties of polycondensed odd-alternant hydrocarbon radicals are still intriguing, especially in view of the design of organic materials with high electric conductivity and organic ferromagnetism. In an effort to approach the radical **1**, we developed a novel synthetic method to extend the π-system of a small odd-alternant hydrocarbon precursor such as phenalenone (**3**).



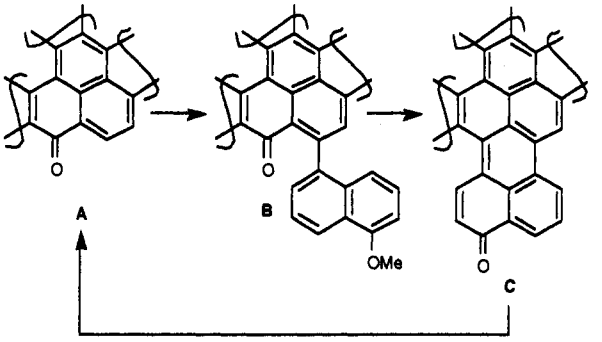
1 2 3

In the first step of the synthesis, the 5-methoxy-1-naphthyl substituent is introduced into the β-position of the cisoid enone in the phenalenone substructure of A to give structure B (Scheme I). In the second step, the carbonyl group in structure B undergoes intramolecular acid-catalyzed condensation with the pendent naphthyl substituent at the position γ to the methoxy group. Since structure C also possesses a phenalenone substructure, it is formally identical with the starting structure A. Consequently, repetition of the process makes it possible to construct polycondensed odd-alternant hydrocarbons. Thus, our new method can be viewed as a "naphthologation" of phenalenone substructure, because the net result is the incorporation of a naphthalene skeleton. Now we would like to demonstrate the feasibility and effectiveness of this new method by the synthesis of 15*H*-benzo[*dc*]naphtho[1,2-*a*]perylen-15-one (**4**), a precursor of the fascinating radical **1**, and 9*H*-benzo[*cd*]perylen-9-one (**5**).

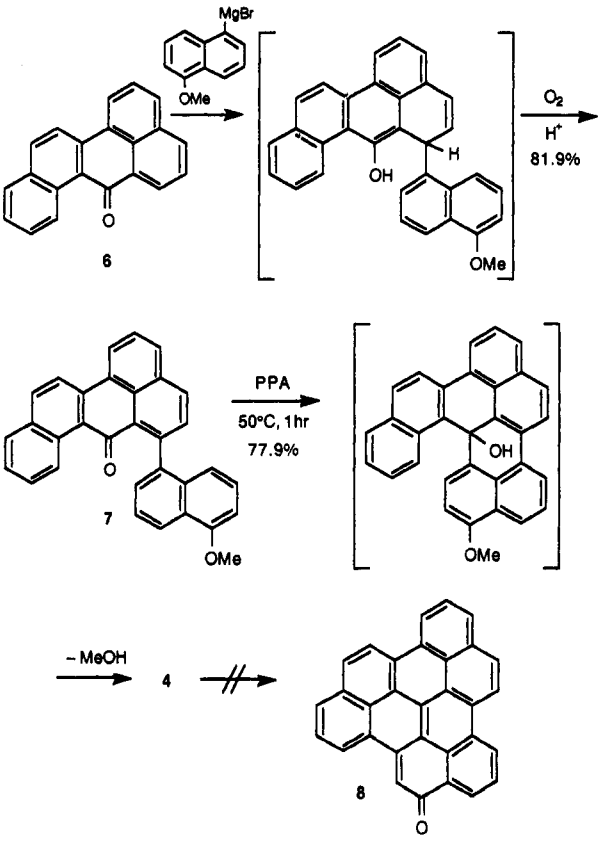
Results and Discussion

6-(5-Methoxy-1-naphthyl)-7*H*-benzo[*hi*]chrysen-7-one (**7**) was prepared by the reaction of 7*H*-benzo[*hi*]-chrysen-7-one (**6**) with (5-methoxy-1-naphthyl)magnesium bromide in toluene at 80 °C and subsequent autoxidation in the presence of hydrochloric acid as illustrated in Scheme II. Intramolecular polyphosphoric acid-catalyzed

Scheme I



Scheme II

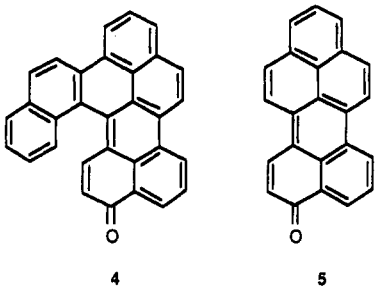


condensation occurred surprisingly readily to give 15*H*-benzo[*dc*]naphtho[1,2-*a*]perylen-15-one (**4**) in 78% yield, despite its strained helicene structure. In this reaction, the methoxy group played a dual role: (1) enhancing the reactivity of the position γ to it and (2) providing a driving force by loss of methanol through a 1,6-elimination. Further ring closure to the structure **8** was attempted under a variety of conditions, such as treatment with $AlCl_3$ or $Pd(OAc)_2$[4] or by photochemical method, but unfortunately all were unsuccessful.

To examine the scope of our new method, we applied it to the parent phenalenone which is supposedly less reactive in the acid-catalyzed condensation than 7*H*-benzo[*hi*]chrysen-7-one (**6**). The 5-methoxy-1-naphthyl group was introduced to phenalenone with the same Grignard reagent as mentioned above. Subsequent oxidation required a strong oxidant, such as DDQ (Scheme III).

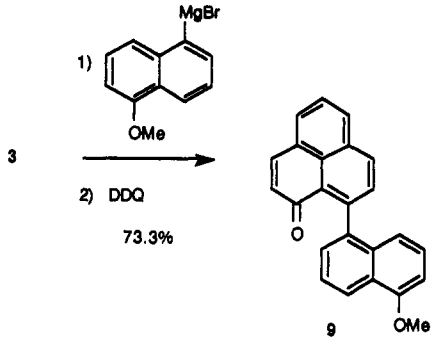
(1) (a) Reid, D. H. *Q. Rev. Chem. Soc.* **1965**, *19*, 274. (b) Murata, I. *Pure Appl. Chem.* **1993**, *65*, 97.
(2) (a) Haddon, R. C. *Aust. J. Chem.* **1975**, *28*, 2343. (b) Gerson, F. *Helv. Chim. Acta* **1966**, *49*, 1463. (c) Hünig, S.; Wolff, E. *Chimia* **1968**, *22*, 33.
(3) (a) Allen, C. F. H. *Can. J. Chem.* **1973**, *51*, 382. (b) Clar, E. *Ber.* **1965**, *65*, 846.
(4) (a) Itahara, T. *J. Chem. Soc., Chem. Commun.* **1981**, 859. (b) Itahara, T.; *Sakakibara, T. Synthesis* **1978**, 607.

0022-3263/93/1958-5846$04.00/0

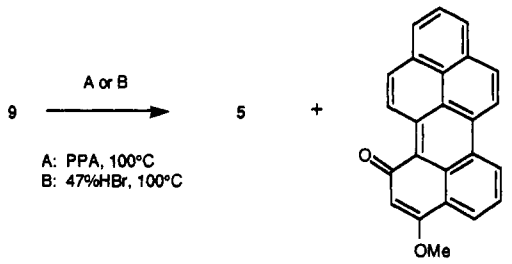


4 5

Scheme III



Scheme IV



A	13.7%	7.7%
B	83.2%	0%

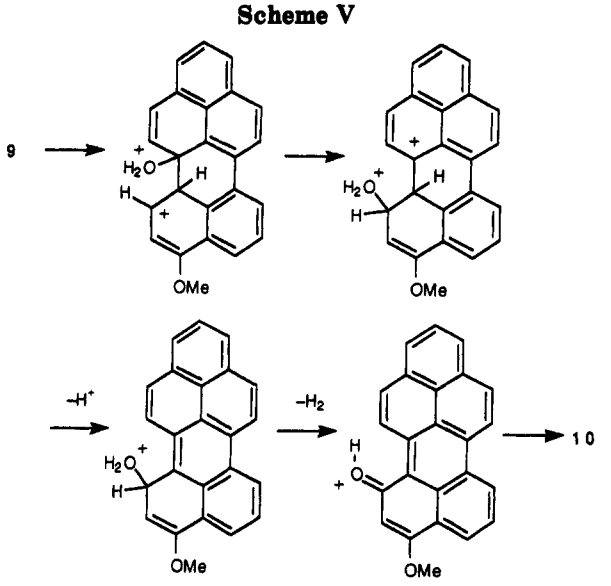
Polyphosphoric acid-catalyzed reaction led to somewhat unexpected results with the formation of side product **10** in a considerable amount (Scheme IV under condition A). The formation of **10** was assumed to occur through 1,3-rearrangement of the protonated hydroxy group with no loss of methanol, as illustrated in Scheme V. Use of 47% hydrobromic acid instead of polyphosphoric acid, however, gave **5** as a sole product cleanly and in high yield (83.2%, Scheme IV under condition B). This difference implies that a bromide ion perhaps behaved as a nucleophile in acidic media to assist extrusion of the methyl group before the 1,3-rearrangement. Investigation on the further extension of the π-system of phenalenone as in Scheme I is now in progress.

Though the application is limited at present, we believe our method would prove useful in construction of the ketone precursor of highly condensed odd-alternant hydrocarbons.

Experimental Section

Melting points are uncorrected. Infrared spectra were recorded on a JASCO IR-700 instrument. ^{1}H NMR spectra were recorded at 400 MHz on a JEOL GX-400 instrument. All assignments were made by means of the COSY-45 technique. Mass spectra were recorded on HITACHI M-60 and JEOL JMS-D300 instruments as indicated. All elemental analyses were performed at the Service Centre of the Organic Compounds (Faculty of Science, Kyushu University).

Scheme V



General Procedure for the Preparation of 7 and 9. A solution of (5-methoxy-1-naphthyl)magnesium bromide in ether was prepared from Mg turnings (45.1 mg, 1.86 mmol) and 1-bromo-5-methoxynaphthalene[6] (389.3 mg, 1.642 mmol) in anhydrous ether (3 mL). Neat 7*H*-benzo[*hi*]chrysen-7-one (**6**)[6] (47.8 mg, 0.171 mmol) (for **9**, phenalenone[7] (90.6 mg, 0.503 mmol) was used) was added to the Grignard solution, refluxing was maintained for 10 min, dry toluene (10 mL) was added, and the mixture was heated to 80 °C for a further 30 min. The reaction mixture was allowed to cool to room temperature and treated with excess 6 N hydrochloric acid for 3 days (for **9**, treated with DDQ (126.6 mg, 0.5576 mmol)). Following separation of the organic phase, washing with water and then $NaHCO_3$ solution, drying (Na_2SO_4), and evaporation gave a brownish red resin. Column chromatography (WAKOgel C-200, elution with toluene) and PTLC (Kieselgel 60PF_{254}, development with *n*-hexane–toluene 1:3) afforded **7** (61.0 mg, 81.9%) (for **9**, 123.9 mg, 73.3%).

7: yellow needles, mp 132–134 °C (from ethanol–chloroform); IR (KBr, cm^{-1}) 1642; MS (recorded on JEOL JMS-D300) *m/e* 436 (M^+); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (d, J = 8.8 Hz, 1H), 8.64 (d, J = 7.8 Hz, 1H), 8.42 (d, J = 9.3 Hz, 1H), 8.41 (d, J = 8.3 Hz, 1H), 8.23 (d, J = 7.8 Hz, 1H), 8.11 (d, J = 7.8 Hz, 1H), 8.10 (d, J = 9.3 Hz, 1H), 7.83 (dd, J = 1.5, 8.8 Hz, 1H), 7.79 (t, J = 7.8 Hz, 1H), 7.69 (d, J = 7.8 Hz, 1H), 7.62 (dd, J = 6.8, 8.3 Hz, 1H), 7.49 (dd, J = 1.0, 6.8 Hz, 1H), 7.47 (m, 1H), 7.42 (m, 1H), 7.22 (d, J = 8.8 Hz, 1H), 7.15 (dd, J = 7.8, 8.8 Hz, 1H), 6.81 (d, J = 7.8 Hz, 1H), 4.07 (s, 3H).

Anal. Calcd for $C_{32}H_{20}O_2$: C, 88.05; H, 4.62. Found: C, 87.83; H, 4.73.

9: yellow needles, mp 202–204 °C (from benzene); IR (KBr, cm^{-1}) 1635; MS *m/e* 335 (M^+ – 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 8.3 Hz, 1H), 8.24 (d, J = 8.3 Hz, 1H), 8.11 (d, J = 8.3 Hz, 1H), 7.82 (d, J = 7.3 Hz, 1H), 7.71 (d, J = 9.3 Hz, 1H), 7.67 (dd, J = 7.3, 8.3 Hz, 1H), 7.64 (d, J = 8.3 Hz, 1H), 7.56 (dd, J = 7.3, 8.3 Hz, 1H), 7.33 (d, J = 7.3 Hz, 1H), 7.17 (t, J = 8.3 Hz, 1H), 6.90 (d, J = 8.3 Hz, 1H), 6.80 (d, J = 8.3 Hz, 1H), 6.50 (d, J = 9.3 Hz, 1H), 4.03 (s, 3H). Anal. Calcd for $C_{24}H_{16}O_2$: C, 85.69; H, 4.79. Found: C, 85.76; H, 4.84.

General Procedure A for the Preparation of 4, 5, and 10. Ketone **7** (45.5 mg, 0.0997 mmol) was dissolved completely in 10 mL of PPA (>75% P_2O_5) to form a purple solution by four addition–evaporation cycles using dichloromethane as solvent. The mixture was stirred at 50 °C for 1 h, poured in small portions onto a saturated KOH solution (60 mL), and extracted with dichloromethane. The fluorescent orange extract was dried with anhydrous Na_2SO_4, passed through a short column (WAKOgel

(5) Hill, P.; Short, F.; Stromberg, H. *J. Chem. Soc.* **1937**, 1619.
(6) Cook, J. W.; de Worms, C. G. M. *J. Chem. Soc.* **1939**, 268.
(7) Lock, G.; Gergly, G. *Ber.* **1944**, *77B*, 461.

C-200), and chromatographed on a PTLC plate (20 cm × 20 cm, Kieselgel 60PF_{254}, CH_2Cl_2) to furnish pure **8** (31.4 mg, 77.9%).

4: brown needles, mp 290–295 °C dec (from chloroform–ethanol); IR (KBr, cm^{-1}) 1629; MS *m/e* 406 ($M^+ + 2$); ^1H NMR (400 MHz, $CDCl_3$) δ 9.29 (d, J = 7.3 Hz, 1H), 8.98 (d, J = 9.3 Hz, 1H), 8.95 (d, J = 7.3 Hz, 1H), 8.87 (d, J = 7.8 Hz, 1H), 8.77 (d, J = 8.8 Hz, 1H), 8.35 (d, J = 9.3 Hz, 1H), 8.26 (d, J = 7.8 Hz, 1H), 8.21 (d, J = 8.8 Hz, 1H), 8.19 (d, J = 8.8 Hz, 1H), 8.09 (t, J = 7.3 Hz, 1H), 8.04 (t, J = 7.8 Hz, 1H), 8.00 (d, J = 7.8 Hz, 1H), 7.80 (d, J = 9.8 Hz, 1H), 7.55 (t, J = 7.8 Hz, 1H), 7.42 (t, J = 8.8 Hz, 1H), 6.55 (d, J = 9.8 Hz, 1H).

Anal. Calcd for $C_{31}H_{16}O$: C, 92.06; H, 3.99. Found: C, 91.69; H, 4.01.

5: red plates, mp 298–300 °C dec (from chloroform); IR (KBr, cm^{-1}) 1631; MS *m/e* 304 (M^+); ^1H NMR (400 MHz, $CDCl_3$) δ 9.33 (d, J = 7.3 Hz, 1H), 9.05 (d, J = 9.3 Hz, 1H), 8.96 (dd, J = 1.5, 7.3 Hz, 1H), 8.79 (d, J = 10.3 Hz, 1H), 8.55 (d, J = 9.8 Hz, 1H), 8.43 (d, J = 9.3 Hz, 1H), 8.33 (d, J = 7.3 Hz, 1H), 8.22 (d, J = 7.3 Hz, 1H), 8.16 (d, J = 9.8 Hz, 1H), 8.05 (t, J = 7.3 Hz, 2H), 6.98 (d, J = 10.3 Hz, 1H).

Anal. Calcd for $C_{23}H_{12}O$: C, 90.77; H, 3.97. Found: C, 90.41; H, 4.01.

10: red plates, mp 259–260 °C dec (from toluene); IR (KBr, cm^{-1}) 1626; MS *m/e* 334 (M^+); ^1H NMR (400 MHz, $CDCl_3$) δ 10.29 (d, J = 9.8 Hz, 1H), 9.08 (d, J = 7.8 Hz, 1H), 8.94 (d, J = 9.3 Hz, 1H), 8.43 (dd, J = 1.5, 7.8 Hz, 1H), 8.35 (d, J = 9.3 Hz, 1H), 8.27 (d, J = 7.8 Hz, 1H), 8.25 (d, J = 9.8 Hz, 1H), 8.21 (d, J = 7.8 Hz, 1H), 8.02 (t, J = 7.8 Hz, 1H), 7.79 (t, J = 7.8 Hz, 1H), 6.29 (s, 1H), 4.06 (s, 3H).

Anal. Calcd for $C_{24}H_{14}O_2$: C, 86.21; H, 4.22. Found: C, 85.91; H, 4.34.

Procedure B for the Preparation of 5. A solution of 9-(5-methoxy-1-naphthyl)phenalenone (102.8 mg, 0.3056 mmol) in 30 mL of 47% hydrobromic acid was heated at 100 °C for 40 min to give dark blue needles. The precipitate was collected by filtration, suspended in an aqueous sodium bicarbonate solution, sonicated, and extracted with chloroform. After the insoluble material was removed by filtration, the extract was dried (Na_2SO_4). Column chromatography (WAKOgel C-200, $CHCl_3$) furnished pure **5** (77.4 mg, 83.2%).

Acknowledgment. This work is supported by a Grant-in-Aid for Scientific Research (No. 04217104) from the Ministry of Education, Science and Culture of Japan. We would like to thank Miss Mie Tomonou (Department of Chemistry, Faculty of Science, Kyushu University) and Dr. Ryuichi Isobe (Faculty of Pharmaceutical Sciences, Kyushu University) for the measurements of mass spectra.

Supplementary Material Available: ^1H NMR spectra and COSY data for all the compounds together with a difference NOE spectrum for **9** and a decoupling spectrum for **5** (12 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.