JOC*Note*

Oxidative Aromatization of 9,10-Dihydroanthracenes Using Molecular Oxygen Promoted by Activated Carbon

Natsuki Nakamichi, Hirotoshi Kawabata, and
Masahiko Hayashi*

Department of Chemistry, Faculty of Science,
Kobe University, Kobe 657-8501, Japan

mhayashi@kobe-u.ac.jp

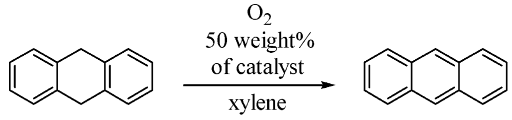
Received July 11, 2003

Abstract: Substituted 9,10-dihydroanthracenes were oxidatively aromatized to the corresponding anthracenes effectively by using molecular oxygen as an oxidant and activated carbon (Darco KB, Aldrich, Inc.) as a promoter in xylene.

The aromatization of polycyclic hydroaromatic compounds such as substituted 9,10-dihydroanthracenes has been investigated so far.[1] Several methods have been reported which include the oxidative aromatization by chloranil[2] or DDQ,[3] the dehydrogenative aromatization by Pd/C,[3,4] and the aromatization employing RhCl-$(PPh_3)_3$,[4] trityl salts,[5] *n*-BuLi/*N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA)/MeI,[6] etc. However, these methods require a stoichiometric or an excess amount of the oxidants in most cases. Furthermore, in some cases an extremely high temperature is necessary. Therefore, a more efficient process using oxygen as an oxidizing agent with the aid of effective catalyst has been desired from an environmental viewpoint. More recently, Yamada reported the oxidative aromatization with oxygen catalyzed by ruthenium porphyrin complex.[7] In this paper, we report an environmentally friendly method for the oxidative aromatization of several 9,10-dihydroanthracenes using molecular oxygen promoted by inexpensive and readily available activated carbon.

We first examined the aromatization of 9,10-dihydroanthracene (**1**) using a Pd/C catalyst.[8] As a result, we found that the reaction using 50 wt % of 10% Pd/C under an oxygen atmosphere in xylene at 120 °C exhibited high performance in this conversion (93% yield, entry 1 in Table 1). When the reaction was carried out in the presence of 50 wt % of Pd black (entry 2), the aromatization proceeded slowly (36% yield) and the starting material was recovered in 63% yield. Based on these results, we assumed that the activated carbon might play an important role in this reaction. Actually, the reaction proceeded by employing the activated carbon without any palladium sources (entry 3). That is, treatment of 9,10-dihydroanthracene (**1**) with 50 wt % of activated carbon (Darco KB, Aldrich, Inc.) in xylene under an oxygen atmosphere at 120 °C for 15 h produced anthracene (**2**) in 93% yield.[9]

TABLE 1. Aromatization of 9,10-Dihydroanthracene

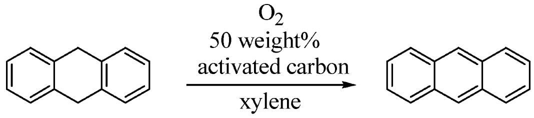


1 **2**

entry	catalyst	yield[b] (%)
1	10% Pd/C	93
2	Pd black	36 (63)
3	activated carbon[a]	93
4	none	8 (92)

[a] Darco KB (Aldrich, Inc.). [b] Determined by ^1H NMR analyses. The values in the parentheses indicate the yield of recovered **1**.

TABLE 2. Effect of Activated Carbon



1 **2**

entry	activated carbon	surface area[a] (m^2/g)	Fe[b] (ppm)	yield[d] (%)
1	Darco KB	1500	299 (N.D.)[c]	85 (14)
2	Darco KB-B	1500	98.3 (100)	91 (8)
3	Darco G-60	600	175 (200)	50 (48)

[a] Data from Aldrich, Inc. [b] Measured by ICP-AES. The values in the parentheses indicate the data from Aldrich, Inc. [c] No data. [d] Determined by ^1H NMR analyses. The values in the parentheses indicate the yield of recovered **1**.

We then examined the aromatization of 9,10-dihydroanthracene (**1**) by using the three types of activated carbon, that is, Darco KB, Darco KB-B, and Darco G-60 (Table 2). It was found that the use of Darco KB and Darco KB-B, which had larger surface area compared to Darco G-60, exhibited higher activity in the conversion of 9,10-dihydroanthracene (**1**) to the corresponding aromatized anthracene (**2**) (entries 1 and 2). We measured the contents of metals in the above three types of activated carbon by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Among the metals we observed, the content of Fe should be noted.[10] That is,

---

* To whom correspondence should be addressed. Fax: +81-78-803-5688.

(1) Fu, P. P.; Harvey, R. G. *Chem. Rev.* **1978**, *78*, 317.

(2) Braude, E. A.; Jackman, L. M.; Linstead, R. P. *J. Chem. Soc.* **1954**, 3564.

(3) Harvey, R. G.; Arzadon, L.; Grant, J.; Urberg, K. *J. Am. Chem. Soc.* **1969**, *91*, 4535.

(4) Blum, J.; Biger, S. *Tetrahedron Lett.* **1970**, *11*, 1825.

(5) (a) Bonthrone, W.; Reid, D. H. *J. Chem. Soc.* **1959**, 2773. (b) Fu, P. P.; Harvey, R. G. *Tetrahedron Lett.* **1974**, *15*, 3217.

(6) (a) Kitamura, M.; Shen, B.; Liu, Y.; Zheng, H.; Takahashi, T. *Chem. Lett.* **2001**, 646. (b) Harvey, R. G.; Cho, H. *J. Am. Chem. Soc.* **1974**, *96*, 2434. (c) Harvey, R. G.; Nazareno, L.; Cho, H. *J. Am. Chem. Soc.* **1973**, *95*, 2376.

(7) (a) Tanaka, H.; Ikeno, T.; Yamada, T. *Synlett* **2003**, *4*, 576. (b) Hashimoto, K.; Tanaka, H.; Ikeno, T.; Yamada, T. *Chem. Lett.* **2002**, 582.

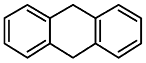
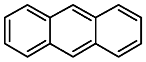
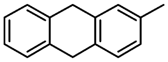
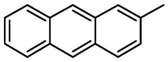
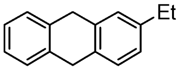
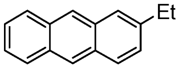
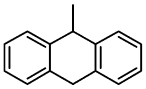
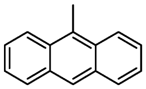
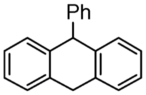
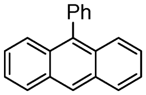
(8) We recently reported the Pd/C catalyzed oxidative aromatization of 1,3,5-trisubstituted pyrazolines and Hantzsch 1,4-dihydropyridines; Nakamichi, N.; Kawashita, Y.; Hayashi, M. *Org. Lett.* **2002**, *4*, 3955.

(9) Only slow conversion was observed even in the absence of catalysts (120 °C, 15 h, 8% yield).

(10) The contents of metals other than Fe in Darco KB which might concern this oxidative aromatization were as follows (ppm): Cu, 16.8 ppm; Mn, 9.99 ppm; Cr, 6.81 ppm. The contents of all metals in Darco KB, Darco KB-B, and Darco G-60 are listed in the Supporting Information.

10.1021/jo034995q CCC: $25.00

TABLE 3. Aromatization of Various 9,10-Dihydroanthracenes[a]

entry	substrate	time (h)	product	yield (%)[b]
1		15		86 (93)
2		24		81 (97)
3		24		90 (99)
4		32		79 (85)
5		24		85 (99)

[a] All reactions were carried out using 200−300 mg of substrate and 50 wt % of activated carbon (Darco KB, Aldrich, Inc.) in xylene (3.5 mL) at 120 °C under an oxygen atmosphere. [b] Isolated yields by recrystallizations. The values in the parentheses indicate the yields determined by ^{1}H NMR analyses.

the following amount of Fe was observed in 1 g of activated carbon: Darco KB, 299 ppm; Darco KB-B, 98.3 ppm; Darco G-60, 175 ppm. Among these activated carbons we examined, Darco KB-B contained a smaller amount of Fe; however, the reactivity of it was almost the same with Darco KB, which contained a larger amount of Fe. In these activated carbons, the important difference is not the amount of Fe but the extent of surface area: Darco KB, 1500 m^2/g; Darco KB-B, 1500 m^2/g; Darco G-60, 600 m^2/g (data from Aldrich, Inc.). Therefore, it would be considered that the extent of the surface area would exhibit more important effect on reactivity than the amount of Fe in the activated carbon. At present, we assume that the activated carbon would effectively adsorb oxygen to promote the reaction.

Several examples of the aromatization of 9,10-dihydroanthracene derivatives to the corresponding anthracenes are summarized in Table 3. The 9,10-dihydroanthracenes bearing a variety of substituents were treated with 50 wt % activated carbon (Darco KB) in xylene under oxygen (120 °C, 15–32 h) to give the corresponding substituted anthracenes in high yield (79−90% yield).

In conclusion, we have disclosed an extremely simple oxidative aromatization method to convert 9,10-dihydroanthracenes to the corresponding anthracenes using molecular oxygen promoted by activated carbon.[11] Further investigations on the detail reaction mechanism including the role of activated carbon are currently underway.

Experimental Section

Typical Procedure for Oxidative Aromatization. A three-necked flask was charged with 9,10-dihydroanthracene (**1**) 2.0 g (11.1 mmol), xylene[12] (15 mL), and 1.0 g (50 wt %) of activated carbon (Darco KB, Aldrich, Inc.) under an oxygen atmosphere using a balloon. The whole was warmed to 120 °C and stirred for 12 h at this temperature. After confirmation of the consumption of starting material by TLC analysis, activated carbon was filtered off using Celite. After washing with toluene, the filtrate was evaporated and the resulting solid was purified by recrystallization to give the desired anthracene (**2**) 1.7 g (86%) as a yellow crystal: mp 216 °C (lit.[13] mp 218 °C).

General Procedure for Measurement of ICP-AES. All reagents used in this study were of analytical or special grade.

Wet digestion method: An accurately weighed activated carbon (1.0 g) was digested with 20 mL of 2 M HNO_3. After the solution was shaken for 24 h at room temperature, activated carbon was removed by filtration. Then, 5 mL of filtrate was diluted with water to 50 mL. The resulting solution was analyzed by ICP-AES (Varian Liberty Series II).

Dry digestion method: An accurately weighed activated carbon (1.0 g) was heated for 6 h at 600 or 800 °C. After the residue was cooled to room temperature, 2 mL of 12 M HCl was added and heated gently. The insoluble material was filtrated, and the filtrate was diluted with water to 100 mL. The resulting solution was analyzed by ICP-AES.

Acknowledgment. This research was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan. We also thank Ms. Yoshiko Murakami of Yamaguchi University for measuring ICP-AES.

Supporting Information Available: Experimental procedures and compound characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

JO034995Q

---

[11] The present activated carbon (Darco KB, Aldrich, Inc.) also promoted the reaction of Hantzsch 1,4-dihydropyridine to afford the corresponding pyridine derivative in high yield. The detail of this reaction will be published soon.

[12] We used an inexpensive mixture of *o*-, *m*-, and *p*-xylene.

[13] *Merck Index*, 13th ed.; Merck: Boca Raton, 2001; p 115.