

Synthesis of Coronene Using Microwave Irradiation

Bing YANG, Ying LI*, Ming Gui XIE

Faculty of Chemistry, Sichuan University, Chengdu 610064

Abstract: Using microwave irradiation, perylene was obtained from 3,4,9,10-perylenetetracarboxylic dianhydride with copper powder in boiling quinoline. With the same method, 1,12-benzoperylene was synthesized from 1, 12-benzoperylene-1', 2'-dicarboxylic anhydride, and coronene was prepared from coronene-1, 2- dicarboxylic anhydride with good yield. Through Diels-Alder reaction, 1, 12-benzoperylene-1', 2'-dicarboxylic anhydride and coronene-1,2-dicarboxylic anhydride were also prepared using microwave irradiation.

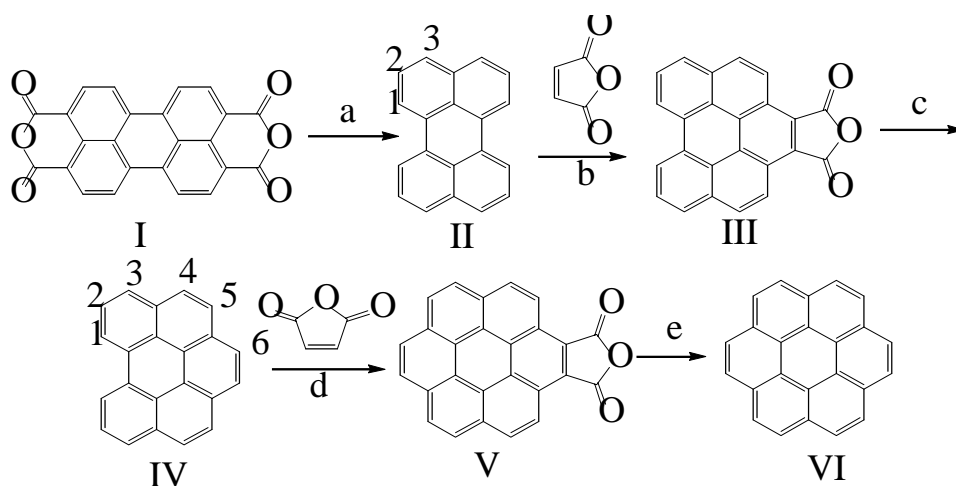
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It was well known that coronene is a very good UV fluorescence material and used widely as organic conductors in solar cell research. Especially in recent years, coronene was used in Ultraviolet Charge Coupled Device (UV-CCD) research¹. As for the synthesis of coronene, three methods were employed: Wurtz-Fittig reaction², Diels-Alder reaction³ and anions reaction⁴. But all of them have some defects. For example, Wurtz-Fittig reaction has very poor yield (4 %). Diels-Alder reaction needs superheating, high vacuum and very long time with the yield of 25 % from perylene. Although anion reaction has higher yield (44 %), its condition is harsh (without oxygen and water at -68°C). Herein, we report a simple method for the synthesis of coronene using microwave irradiation. The synthetic route was shown in **Scheme 1**.

Results and Discussion

As quinoline⁵ could act as good catalyst in decarboxylation, we achieved the conversion of 3,4,9,10-perylenetetracarboxylic dianhydride **I** into perylene **II** with copper powder in quinoline under microwave irradiation (850 W) for 8 h, and the yield was up to 65 %. Van Dijk⁴ reported that this synthesis has to be performed at 380°C for 5 ~ 7 days with the yield of 80 %. With the same method, 1,12-benzoperylene-1', 2'-dicarboxylic anhydride **III** also could be converted into 1, 12-benzoperylene **IV** and coronene-1,2-dicarboxylic anhydride **V** could be converted into coronene **VI**. The yields were 80 % and 86 % respectively and the reaction time was only 5 hours, while Clar has reported³

*E-mail: ybice@263.net

Scheme 1 The synthetic route of coronene

Reagents and conditions: a). Cu, quinoline, microwave irradiation, 850W, 8h, yield: 65%. b): nitrobenzene, microwave irradiation, 850W, 30min, yield: 96%. c): Cu, quinoline, microwave irradiation, 850W, 5h, yield: 80%. d): nitrobenzene, microwave irradiation, 850W, 1h, yield: 10%. e): Cu, quinoline, microwave irradiation, 850W, 5h, yield: 86%.

that these conversions need superheating and vacuum condition for about 9 hours with the yield of 40 %. Under the microwave irradiation, **II** with maleic anhydride in boiling nitrobenzene that was used as an oxidizing reagent, could be easily converted to **III** with yield of 96 %. Under the same reaction condition, the conversion of **IV** into **V** also could achieve but the yield was low (about 10 %). Clar reported that this conversion was not available³ at his condition.

Experimental

Microwave oven (made by Whirlpool Com.) was used. Mass spectra data were recorded on a Finnigan MAT-4510 spectrometer. ¹H NMR spectra were recorded on Bruker DP-400 MHz. M.P. was taken in evacuated capillaries and the thermometer was not revised. All the chemicals and reagents were obtained commercially and used without further purification.

Perylene II: 10 g (25.5 mmol) of **I** was dissolved in 150 mL quinoline with 0.5 g copper powder. Then the mixture was irradiated by microwave (850 W) for 8 h. Copper powder was filtered off and the solvent was evaporated *in vacuo*. The residue was crude product as a yellow solid and purified by column chromatography on silica gel, using toluene-dichloromethane (1:1) as the eluent. 4.2 g of perylene was obtained (yield: 65 %).

1,12-Benzoperylene-1', 2'-dicarboxylic anhydride III: 3 g (12 mmol) perylene and 1.2 g (12 mmol) maleic anhydride were dissolved in 30 mL nitrobenzene and irradiated

(850 W) for 30 min in the microwave oven. The red brown anhydride was crystallized from the solution, recrystallized from xylene. 4 g pure **III** was obtained (yield: 96 %).

1,12-Benzoperylene **IV**: 3 g **III** (8.7 mmol) was dissolved in 30 mL quinoline with 0.1 g copper powder. The reaction mixture was irradiated for 5 h and purified according to the procedure described above. 1.9 g of benzoperylene was obtained (yield: 80 %).

Coronene-1,2-dicarboxylic anhydride **V**: 1 g (3.7 mmol) benzoperylene was dissolved in 10 mL nitrobenzene with 0.4 g (4 mmol) maleic anhydride. The mixture was irradiated for 1 h, 0.1 g of **V** was obtained (yield: 10 %). **V** could be also obtained *via* the methods in ref.⁴ with the yields of 62 %.

Coronene **VI**: According to the procedure for preparation of **IV**, 0.5 g (1.4 mmol) **V** could be converted into 0.3 g coronene (yield: 86 %).

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References and Notes

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6. Data: **II**: ¹H NMR (CDCl₃, δ ppm): 7.457 ~ 7.496 (t, 4H, J= 8 Hz, 7.6 Hz, H-2), 7.667 ~ 7.687 (d, 4H, J= 8 Hz, H-3), 8.178 ~ 8.198 (d, 4H, J= 8 Hz, H-1); MS. (*m/z*, %): 252 (M⁺, 64); m.p.: 268°C (lit.³: 268°C ~ 269°C). **III**: MS (*m/z*): 346 (M⁺, 11). **IV**: ¹H NMR (CDCl₃, δ ppm): 8.000 ~ 8.039 (t, 2H, J= 8 Hz, 7.6 Hz, H-2), 8.074 ~ 8.096 (d, 2H, J= 8.8 Hz, H-2), 8.123 ~ 8.145 (d, 2H, J= 8.8 Hz, H-4), 8.184 ~ 8.205 (d, 2H, J= 7.6 Hz, H-3), 8.352 (s, 2H, H-6), 9.000 ~ 9.021 (d, 2H, J= 7.8 Hz, H-1); MS. (*m/z*, %): 272 (M⁺, 98); m.p.: 272°C (lit.³: 273°C). **V**: MS (*m/z*): 370 (M⁺, 19). **VI**: ¹H NMR (CDCl₃, δ ppm): 8.870 (s, 12H); MS (*m/z*, %): 300 (M⁺, 50); m.p.: 424°C~426 °C (lit.³: 425°C ~ 428°C).

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