

Photo precursor for pentacene

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Abstract—6,13-Dihydro-6,13-ethanopentacene-15,16-dione gave pentacene efficiently both in solid and in solution by irradiation of light.

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Pentacene is one of the most sensational polycyclic hydrocarbons, which draws attention from many fields due to its high electron mobility.¹ Many efforts have been focused on the device preparation of not only pentacene² itself but also its derivatives.³ For the application of pentacene and its derivatives, one of the biggest problem is the low solubility in common solvents. Difficulties are often encountered in the purification of its derivatives, and several manipulations of a high vacuum sublimation are required. In the final stage of pentacene-based devices, the vapor deposition technique under high vacuum is usually employed. In order to overcome the problem, precursors, which give pentacene or its derivatives by thermal decomposition, namely retro-Diels–Alder reaction, were developed and their applications for field effect transistors (FET) and organic thin film transistors (OTFT) were recently reported.⁴ In these cases, retro Diels–Alder reaction of the precursors was designed to proceed at rather low temperatures by extrusion of tetrachlorobenzene^{4a} and *N*-sulfinylacetamide.^{4b} The requisite for such leaving molecules is sufficiently small and inert not to affect the property of pentacene devices. For these precursor methods, there is an inevitable drawback that the high vacuum sublimation technique, one of the most reliable and successful device preparation methods, cannot be applied, because

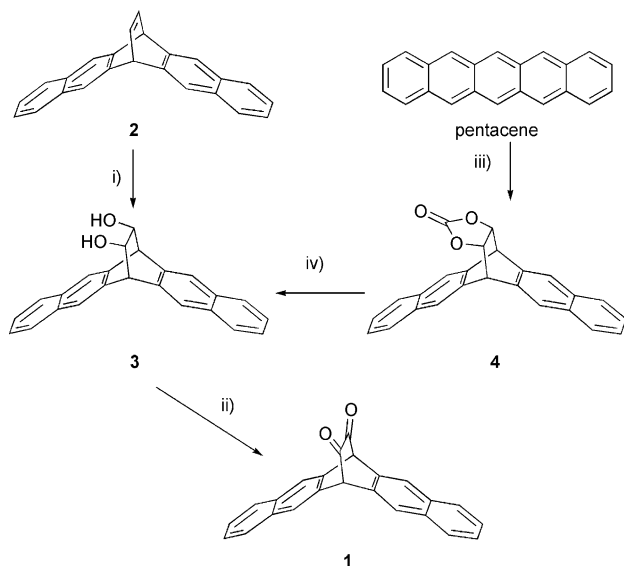
the trigger of the precursors to pentacene is heat. We thought that not only this shortcoming of the precursor method but also property of the leaving molecules can be dramatically improved if the alternative physical decomposition method, namely light, is applied.⁵ In this communication, we report preparation of the first photo-convertible precursor to pentacene and its fundamental properties.

From the Woodward–Hoffmann rule, the retro-Diels–Alder reaction is the $[4\pi+2\pi]$ reaction and the suprafacial reaction mode is thermally allowed, while the $[4\pi]$ suprafacial reaction is not thermally but photochemically allowed. From the correlation diagram of the orbitals, however, some thermally allowed reactions such as the retro $[4\pi+2\pi]$ reaction may be accelerated by irradiation of light.⁶ Since photochemical reactions of bicyclo[2.2.2]octa-2,5-diene-7,8-dione derivatives were regarded as such a concerted process and the extruded ethene-1,2-dione molecule, $O=C=C=O$, readily decomposed into two molecules of carbon monoxide,⁷ we focused on preparation of the dicarbonyl-bridged precursor **1** (Scheme 1).

According to the literature, 6,13-dihydro-6,13-ethenopentacene (**2**) was prepared in 31% overall yield.^{4a,8} Dihydroxylation of the etheno bridge of **2** with OsO_4 gave diol **3** in good yield. Swern oxidation of the diol **3** under the normal conditions [$DMSO$, $(COCl)_2$] gave a poor result and none of the oxidation product was obtained. On the other hand, the diol **3** was readily

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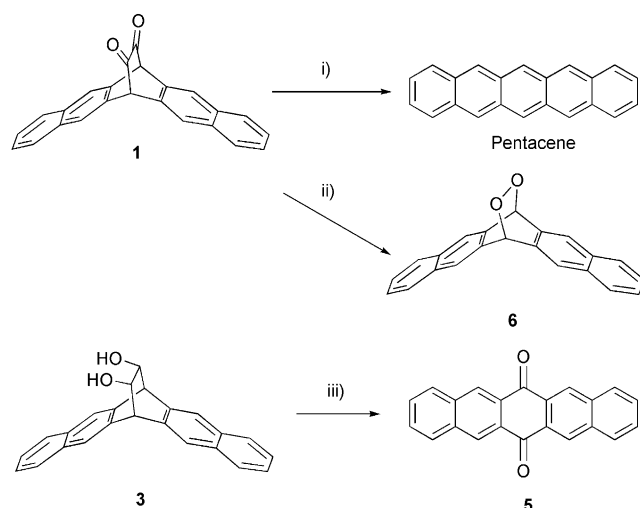
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Scheme 1. Reagents, conditions, and yields: (i) OsO₄, NMO, acetone, rt; 98%; (ii) DMSO, TFAA, Et₃N, CH₂Cl₂, -60 °C; 43%; (iii) vinylene carbonate, xylene, 170 °C; 80%; (iv) NaOH, EtOH, reflux; 90%.

oxidized to the targeted dione **1**⁹ under the modified conditions,¹⁰ though the yield was rather low (43%). The diol **3** was also prepared by Diels–Alder reaction of pentacene with vinylene carbonate followed by hydrolysis in 72% yield. From the UV–vis experiment, the diketone **1** has an absorption peak maximum at 463 nm (ϵ 1400) attributable to $n-\pi^*$ transition. Fortunately, pentacene itself has no strong absorption around this region.

Photochemical conversion of **1** by using a high-pressure Hg lamp (light less than 390 nm was cut by a filter) was carried out in toluene under inert conditions (Scheme 2). Evolution of gas occurred and then, deep violet-blue



Scheme 2. Decomposition of diketone **1** and diol **3**. Reagents, conditions, and yields: (i) $h\nu$, toluene, rt, 74%. (ii) $h\nu$, O₂, toluene, rt, quant. (iii) NaH, DMF, 100 °C, 89%.

leaflets gradually appeared in the solution. Spectroscopic and physical data of the obtained violet-blue crystals are identical with those of commercially available pentacene. The isolated yield of pentacene by simple filtration was 74%. The UV–vis spectra of the filtrate revealed the presence of 6,13-pentacenequinone (**5**), which would be formed by the photochemical reaction of pentacene with a tiny amount of oxygen existed in the solution. Any other by-product could not be detected from the filtrate. In order to clarify the by-product formation, the photo conversion of **1** by irradiation of 460 nm light (xenon lamp) was examined in CDCl₃ in the presence of oxygen and the progress of the reaction was monitored by UV and ¹H NMR (Fig. 1). In this experiment, no formation of pentacene was detected, but *endo*-peroxide **6**¹¹ was formed quantitatively. The similar *endo*-peroxide formation was reported in the photo oxidation of pentacene and its derivatives with oxygen and then the *endo*-peroxides decomposed to the corresponding quinones.¹⁰ The photo-decomposition of **1** was also achieved without solvents. When the light was irradiated to a deposited sample of **1** on a glass, violet-blue color of pentacene appeared (Fig. 2).

Thermal behaviors of **1** and **3** were examined. From the TG-DTA experiments, **1** started to evaporate before obvious decomposition and a sharp drop of weight was observed over 350 °C, while **3** showed rather complexed decomposition accompanied with sublimation. Pentacene could not be obtained in a pure form by the

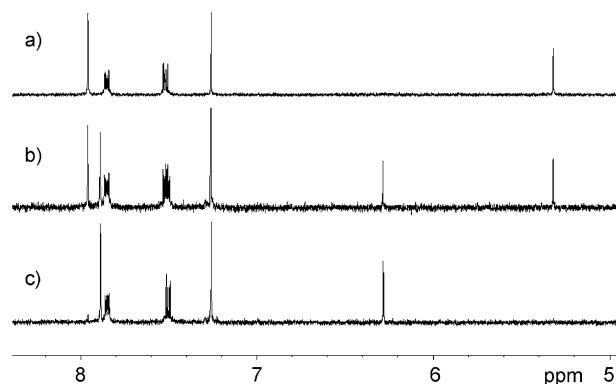


Figure 1. ¹H NMR spectra during the photo decomposition of **1** in the presence of oxygen. (a) Starting **1**; (b) after 1 h; (c) after 2 h.

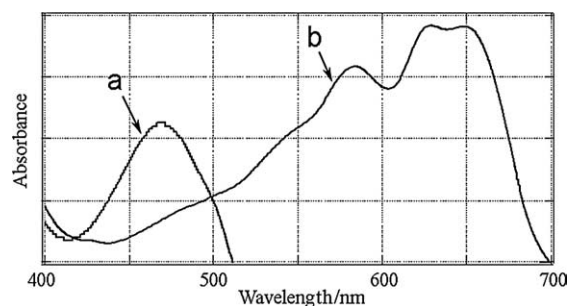


Figure 2. UV–vis spectra of diketone **1** (a: in chloroform) and the photo-converted sample (b: solid on a glass).

thermal decomposition of **3**. When the sodium salt of **3** was heated at 100 °C in DMF,¹² the obtained product was 6,13-pentacenequinone (**5**, 89%) probably due to air oxidation of pentacene formed.

In conclusion, we achieved the first preparation of the readily soluble and stable photo precursor of pentacene, and showed the efficient conversion to pentacene both in solid and in solution. This method provides not only a new synthetic method of pentacene derivatives, which are not easily accessible due to low solubility and stability, but also new preparative methodology for the pentacene-based devices. Further studies about the device preparation are under way.

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9. *Selected data for 1*: Yellow crystals, mp 320 °C; ¹H NMR δ (CDCl₃) 7.94 (4H, s), 7.84 (4H, m), 7.52 (4H, m) and 5.31 (2H, s); ¹³C NMR δ (CDCl₃) 185.2, 133.6, 131.9, 127.9, 127.0, 125.4, and 60.6; IR (KBr) 1755, 1736, and 756 cm⁻¹; UV-vis (ε, CHCl₃) 463 (1400) nm.
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