Synthesis of 4*H*-Cyclopenta[*def*]phenanthrene from 1-Naphthylacetic Acid

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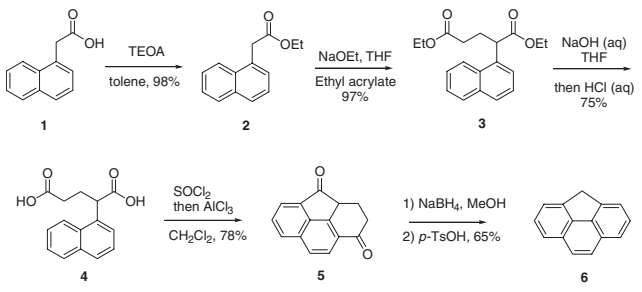
4*H*-cyclopenta[*def*]phenanthrene (CPP) was prepared from 1-naphthylacetic acid in six steps with an overall yield of 36%. From easily available ethyl 1-naphthaleneacetate, the Michael addition and Lewis acid catalyzed dicyclization provided the diketone, which was reduced and dehydrated to give CPP.

Stabilized blue emission from of polymeric organic light emitting diodes (OLED) has been a great challenge to overcome.[1,2] OLEDs with dialkyl-substituted poly(4*H*-cyclopenta[*def*]phenanthrene) (PCPP) have shown outstanding stability of blue emission even after annealing or operation of the device in air.[2] The 4*H*-cyclopenta[*def*]phenanthrene (CPP), used as the starting material for the synthesis of PCPP, was originally isolated in 1934 by Kruber[3] from a refined neutral fraction of anthracene oil. The exceedingly high price of CPP is possibly caused by the very low overall yield of the known preparative method.[4,5] Harvey et al.[4] have prepared CPP from acenaphthene in seven steps with an overall yield of 33%. Here, the improved synthetic method of CPP from 1-naphthylacetic acid, which is much cheaper than acenaphthene, by six steps with an overall yield of 36% is reported.[6]

It was envisioned to synthesize CPP from diketone **5**. Reduction of diketone **5** with $NaBH_4$ followed by treatment with acid provided CPP.

As shown Scheme 1, commercially available 1-naphthylacetic acid (**1**) was protected using triethyl orthoacetate to afford ethyl 1-naphthaleneacetate (**2**).[7] Compound **2** was mono-alkylated using ethyl acrylate in the presence of small amounts of sodium ethoxide by a Michael addition to generate diethyl 2-(1-naphthyl)pentanedioate (**3**) with 97% yield without any noticeable amount of dialkylated by-product. Compound **3** was hydrolysed with aqueous NaOH followed by acidification with aqueous HCl solution to generate 2-(1-naphthyl)pentanedioic acid (**4**).[8] The dicarboxylic acid **4** was treated with thionyl chloride followed by aluminum chloride for the simultaneous formation of five- and six-membered rings to generate compound **5** in 78% yield. The reduction of diketone **5** using sodium borohydride in methanol followed by treatment with *p*-TsOH in toluene provided CPP (**6**) in 65% yield.



Scheme 1. Synthesis of CPP (**6**) from **1**.

In summary, this paper describes the synthesis of CPP from commercially available 1-naphthylacetic acid.[9] CPP was prepared by a convenient route in six steps with an overall yield of 36% utilizing the Michael addition and Lewis acid catalyzed dicyclization.

This work was supported by the Ministry of Information & Communications, Korea, under the Information Technology Research Center (ITRC) Support Program and International Cooperation Research Program of the Ministry of Science & Technology, Korea (Global Research Laboratory, K20607000004-09A0500-00410).

References and Notes

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6 Contrast to the previously reported method,[4,5] the simultaneous formation of five- and six-membered rings is essential for the increase of the overall yield.

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9 A typical experimental procedure is given in the Supporting Information, available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

Published on the web (Advance View) September 12, 2009; doi:10.1246/cl.2009.1008