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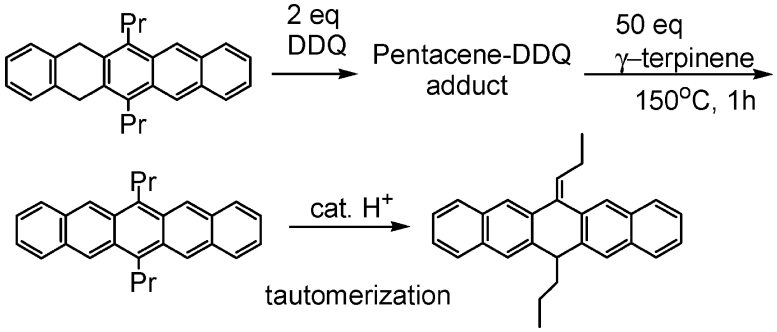

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Isolation of 6,13-Dipropylpentacene and Its Tautomerization

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For aromatic tautomerization between methylacenes and methylenedihydroacenes, the first evidence of an isolable tautomer was reported by Clar and Wright in 1949 in the case of 6-methylpentacene **1** and 6-methylene-6,13-dihydropentacene **2**.[1] They reported that there was an equilibrium between **1** and **2** and that **2** was entirely formed at room temperature.[1] It is well-known that, for example, toluene is much more stable than its tautomer, isotoluene. With an increase of the number of aromatic rings of methylacenes, the difference of ΔH_f values between methylacenes and methylenedihydroacene decreases. Theoretical calculations showed the ΔH_f of **2** was lower than **1** with 8.9 kcal/mol by the MNDO method.[2] This is the explanation of the predominant existence of **2** over **1** in the equilibrium mixture. The heating of **2** at 200 °C afforded **1** in detectable amounts by UV spectroscopy. However, the aromatic compound, 6-methylpentacene **1**, has not been isolated, to the best of our knowledge. Similarly, 6,13-dialkylpentacene such as 6,13-dipropylpentacene **3** is comparably unstable or even more unstable than the corresponding tautomer,[3] 6-propylidene-13-propyl-6,13-dihydropentacene **4** (Figure 1). This type of pentacene derivatives have not been synthesized nor isolated,[4] although many examples are known for 6,13-disubstituted pentacene derivatives.[5−8] This situation prompted us to prepare 6,13-dipropylpentacene **3** to examine whether the aromatic derivative **3** was stable and isolable at room temperature or not.

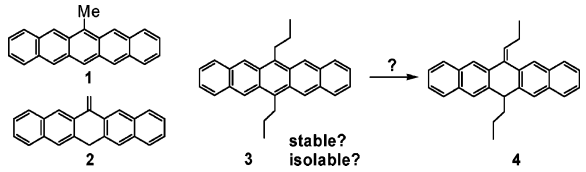


Figure 1. Alkyl-substituted pentacenes **1** and **3** and their tautomers **2** and **4**.

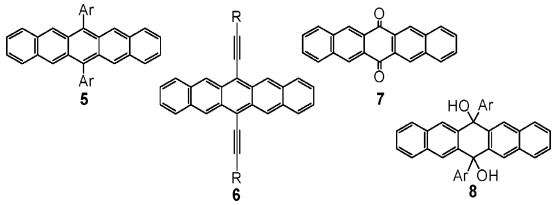
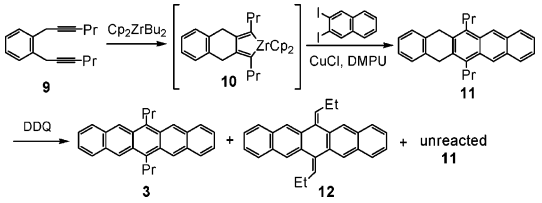


Figure 2. 6,13-Disubstituted pentacenes **5** and **6** and their starting compound **7** and intermediate **8** for **5**.

Scheme 1. Preparation of 6,13-Dipropyl-5,14-dihydropentacene **11** and Its Aromatization with DDQ



6,13-Diarylsubstituted pentacenes **5** and 6,13-dialkynylsubstituted pentacenes **6** have been prepared since 1942 and 1969 by Allen and Maulding, respectively[5,6] (Figure 2). Usually, 6,13-disubstituted pentacenes **5** and **6** have been prepared from pentacenequinone **7** and the corresponding organometallic reagents such as aryl Grignard reagent or alkynyl Grignard reagents. Diols such as **8** were formed as intermediates after the reaction of **7** with aryl Grignard reagents followed by protonolysis. Dehydroxylation from the diols afforded disubstituted pentacenes **5** and **6**.[4,5]

In a similar way to those 6,13-disubstituted pentacene derivatives, a reaction of propyl Grignard reagent with pentacenequinone was carried out. The NMR spectra of the reaction mixture after hydrolysis showed the formation of a mixture of many undefined species. Subsequent dehydroxylation treatment of the mixture with $SnCl_2$ did not give **3** at all.

We turn our attention from pentacenequinone to our coupling reaction of zirconacyclopentadienes for the preparation of **3**.[9] We have developed coupling reactions of zirconacyclopentadienes[9] with diiodobenzene in the presence of CuCl for the aromatic ring extension. As shown in Scheme 1, diiodonaphthalene[10] was used in this case.

6,13-Dipropyl-5,14-dihydropentacene **11** was prepared in 32% isolated yield by the reaction of zirconacyclopentadiene with diiodonaphthalene in the presence of CuCl as shown in Scheme 1. The dihydropentacene **11** was treated with 1 equiv of DDQ at 100 °C. A mixture of **3**, **12**, and the starting material **11** was obtained. Bis(propylidene) derivative **12** was separated by column chromatography. However, unfortunately, it was difficult to separate **3** from **11**. It is consistent with the observation of difficult separation for other multiaromatic compounds from its dihydro derivatives.

For the separation of dihydropentacene and pentacene derivatives, we developed a novel method. It involves (1) the direct formation of pentacene-DDQ adduct by the reaction of dihydropentacene derivatives with an excess of DDQ[11] in order to consume the dihydropentacene derivatives and (2) abstraction of DDQ from the pentacene-DDQ adduct to afford pentacenes cleanly.

To find a suitable reagent for DDQ abstraction from the DDQ adduct of pentacene, we used 1,4,6,13-tetrabutyl-2,3-bis(methoxycarbonyl)-5,14-dihydropentacene **13** as a representative dihydropentacene.[4b] Table 1 shows the result.

Abstraction reaction of DDQ from **14** was carried out with dihydroanthracene **17**, tetralin **18**, γ-terpinene **19**, and α-terpinene **20**. As shown in Table 1, dihydroanthracene and tetralin gave undesired **16** in more than 30% yields. The best result was obtained

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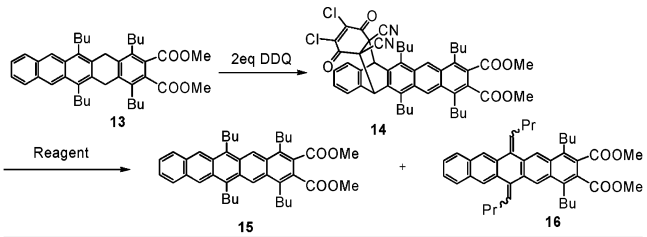
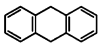
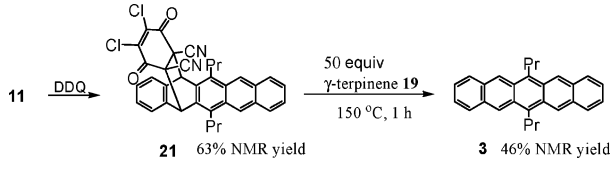
Table 1. DDQ Abstraction from Pentacene-DDQ Adduct **14** for the Formation of Pentacene Derivative **15**



Entry	Reagent		Equiv	Temp /°C	Time /h	remained **14**	**15**	**16**
1		**17**	10	100	3	9	68	32
2		**18**	50	100	3	36	0	36
3		**19**	1.1	100	1	41	42	13
4	**19**		10	100	1	0	95	5
5	**19**		50	80	3	0	100	0
6		**20**	50	80	3	0	93	0

Scheme 2. Reaction of Pentacene-DDQ Adduct **21** with γ-Terpinene



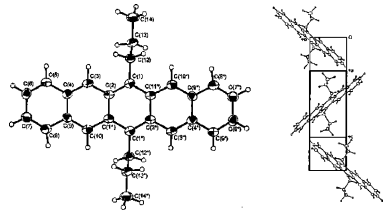


Figure 3. Perspective view of dipropylpentacene **3** and its packing system.

with 50 equiv of γ-terpinene **19** at 80 °C for 3 h. The desired pentacene **15** was obtained in 100% yield without unreacted **14** and **16**.

6,13-Dipropyldihydropentacene was aromatized by this system as shown in Scheme 2. DDQ adduct **21** was prepared first by the reaction of **11** with 2 equiv of DDQ. The DDQ adduct **21** was obtained in 63% NMR yield with complete consumption of **11**.

The adduct was first treated with **19** at 80 °C in toluene. Since the reaction was slow, the reaction was carried out at 150 °C in mesitylene for 1 h. NMR spectra of the reaction mixture revealed that dipropylpentacene **3** was formed in 46% yield. After removal of all solvents and volatile compounds in vacuo, degassed methanol was added to the mixture to remove dihydroquinone and alkylidene derivatives. Thus obtained solid was crystallized from hexane. Blue crystals were obtained in 32% yield.

Its structure was determined by X-ray analysis. The structure is shown in Figure 3. ^{1}H NMR spectrum of **3** showed a singlet signal at 8.93 ppm assigned to four protons of the second aromatic ring from both ends. Signals of eight protons of two side rings appeared at 7.33 and 7.97 ppm. ^{13}C NMR showed 3 CH aromatic ring carbons at 123.7, 125.1, and 128.6 ppm. Three Pr carbons appeared at 15.0, 24.8, and 31.1 ppm assignable to Me, CH_2, and CH_2 attached pentacene skeleton, respectively.

These spectra clearly showed that this compound **3** is stable under N_2 at room temperature. Formation of its tautomer **4** was not observed.

Dipropylpentacene **3** was stable even at 150 °C in mesitylene. On the other hand, when a catalytic amount of camphor-10-sulfonic acid (CSA, 0.15−1.7 mM) was added to a solution of **3** (4.13 mM) at 140 °C in 1,1,2,2-tetrachloroethane-d_2, the tautomerization occurred. The kinetic study revealed the tautomerization from **3** to **4** obeyed second-order rule dependent on the concentrations of pentacene **3** and CSA. The second-order rate constant was 1.03×10^2 M^{-1} min^{-1}. This result showed that tautomerization was catalyzed by CSA. Our successful isolation of pentacene **3** can be attributed to milder reaction conditions of our new aromatization method than the conventional ones such as dehydroxylation with $Sn(II)Cl_2$ or dehydration under acidic conditions, as described before. Obviously, such acidic aromatization would easily cause the tautomerization of 6-alkylated pentacenes and result in failure of its isolation.

Very recently Houk et al. reported the bimolecular hydrogen transfer mechanism for the isomerization from **1** to **2**.[2c] We must await for further investigation if bimolecular hydrogen transfer is available for dipropylpentacene **3**.

Supporting Information Available: Experimental procedure and spectra data for **3**, **4**, **11**, **14**−**16**, and **21**; kinetic study data for tautomerization from **3** to **4**; Crystallographic data for **3** (cif). This material is available free of charge via the Internet at http://pubs.acs.org.

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(3) Our preliminary calculation by the MNDO method showed almost the same ΔH_f values 104.0 and 95.1 kcal/mol for 6-methylpentacene and 6-methylene-6,13-dihydropentacene, respectively, as reported in ref 2b. By this method we calculated for 6,13-dipropylpentacene and 6-propylidene-13-propyl-6,13-dihydropentacene and the ΔH_f values, 91.7 and 78.7 kcal/mol were obtained, respectively.

(4) Multisubstituted pentacenes with alkyl substituents at 6,13-positions, see (a) Takahashi, T.; Kitamura, M.; Shen, B.; Nakajima, K. *J. Am. Chem. Soc.* **2000**, *122*, 12876. (b) Takahashi, T.; Li, S.; Huang, W.; Kong, F.; Nakajima, K.; Shen, B.; Ohe, T.; Kanno, K. *J. Org. Chem.* **2006**, *71*, 7967−7077.

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