ORGANIC
LETTERS

2011
Vol. 13, No. 10
2758–2761

Facile Synthesis of Picene from 1,2-Di(1-naphthyl)ethane by 9-Fluorenone-Sensitized Photolysis

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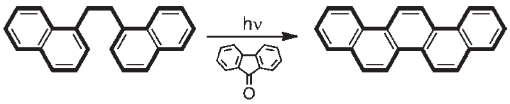
Received April 4, 2011

ABSTRACT



A facile formation of picene was achieved by photosensitization of 1,2-di(1-naphthyl)ethane using 9-fluorenone as a sensitizer. This sensitized photoreaction is the first photochemical cyclization of ethylene-bridged naphthalene moieties to afford the picene skeleton. 5,8-Dibromopicene, prepared by this procedure using 1,2-di[1-(4-bromonaphthyl)]ethane as the substrate, was readily converted to novel functionalized picenes by conventional substitution and cross-coupling reactions.

Aromatic compounds possessing extended π-conjugation have attracted significant attention because of their potential for use as organic electronic materials.[1] In the past decade, pentacene **1** has been widely used as an active layer in organic thin-film field-effect transistors (FETs). However, because pentacene is quite unstable upon exposure to light and air, a number of issues arise, which need to be resolved for its practical application in devices.

Picene **2**, an isomer of pentacene **1** (Figure 1), has been known as a stable compound in which the benzene rings are fused in a zigzag phenacene structure. However, phenacenes have attracted less attention as organic electronic materials than acenes, typified by pentacene **1**.

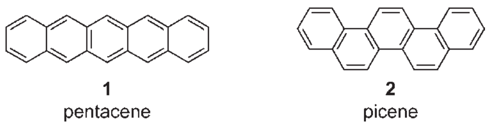


Figure 1. Structures of pentacene **1** and picene **2**.

In a previous report by the current authors, it was shown that picene **2** could serve as an active layer of a high-performance *p*-channel organic thin film FET with a very high field-effect mobility: $\mu \sim 5\ \mathrm{cm^2\,V^{-1}\,s^{-1}}$.[2] Additionally, the reported picene thin film FET was remarkably sensitive to O_2; thus, the FET device responded to O_2 at pressures as low as 10 ppm of O_2 gas.[2a] The picene thin film FET also displayed appreciable hysteresis in the forward and reverse transfer curves under high humidity.[2a] That study, therefore, demonstrated that picene thin film FETs were potentialy applicable to practical organic electronic devices

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(1) Yamashita, Y. *Sci. Technol. Adv. Mater.* **2009**, *10*, 024313.

(2) (a) Okamoto, H.; Kawasaki, N.; Kaji, Y.; Kubozono, Y.; Fujiwara, A.; Yamaji, M. *J. Am. Chem. Soc.* **2008**, *130*, 10470. (b) Kawasaki, N.; Kubozono, Y.; Okamoto, H.; Fujiwara, A.; Yamaji, M. *Appl. Phys. Lett.* **2009**, *94*, 043310. (c) Kaji, Y.; Mitsuhashi, R.; Lee, X.; Okamoto, H.; Kambe, T.; Ikeda, N.; Fujiwara, A.; Yamaji, M.; Omote, K.; Kubozono, Y. *Org. Electron.* **2009**, *10*, 432. (d) Kaji, Y.; Kawasaki, N.; Lee, X.; Okamoto, H.; Sugawara, Y.; Oikawa, S.; Ito, A.; Okazaki, H.; Yokoya, T.; Fujiwara, A.; Kubozono, Y. *Appl. Phys. Lett.* **2009**, *95*, 183302. (e) Lee, X.; Sugawara, Y.; Ito, A.; Oikawa, S.; Kawasaki, N.; Kaji, Y.; Mitsuhashi, R.; Okamoto, H.; Fujiwara, A.; Omote, K.; Kambe, T.; Ikeda, N.; Kubozono, Y. *Org. Electron.* **2010**, *11*, 1394.

10.1021/ol200874q

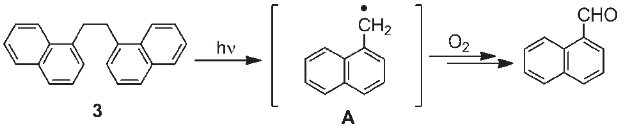
such as gas sensors.[2] Furthermore, picene **2** showed superconductivity with a high superconducting transition temperature, $T_c = 18$ K, upon being doped with alkaline metals such as potassium.[3] The potassium-doped picene is the first hydrocarbon-based superconductor[3] illustrating that picene **2** and its derivatives represent a novel and promising class of materials for organic electronics, although picene has rarely been applied to practical electronic devices.

The conventional synthetic methods employed in the preparation of picene involve the use of multistep procedures.[4] Therefore, a simple and convenient strategy for the synthesis of picene **2** is highly desirable in order to promote further investigations into its use in organic electronics.

In the course of our synthetic study of picene **2**, we have found that sensitized photolysis of 1,2-di(1-naphthyl)-ethane **3** unexpectedly produced picene **2** in one step. Herein, we report the photochemical formation of picene **2** as a new and convenient methodology for picene synthesis. Additionally, the preparation of novel functionalized picenes, with the aim of developing a new phenacene for potential use as an organic electronic material, is also described.

The initial investigations were performed using direct irradiation of dinaphthylethane **3**. When dinaphthylethane **3** was irradiated (>280 nm) in degassed acetonitrile (MeCN), no appreciable product formation was observed. In contrast, photolysis of the same in aerated MeCN resulted in the formation of 1-naphthaldehyde, instead of the desired picene **2**, as observed in the absorption spectra of the photolysate (Figure S1, Supporting Information). It can be concluded that upon direct photolysis, homolytic cleavage of the C–C bond of the ethylene bridge of dinaphthylethane **3** occurred to afford the 1-naphthylmethyl radical **A** which was trapped with the dissolved O_2 and finally produced 1-naphthaldehyde (Scheme 1).[5]

Scheme 1. Direct Photolysis of Dinaphthylethane **3**



Subsequently, the sensitized photolysis of dinaphthylethane **3** was performed using xanthone (**XT**), benzophenone (**BP**), 9-fluorenone (**9F**), and 9,10-dicyanoantharacene (**DCA**) as sensitizers. Primary screening was carried out by monitoring the progress of the photoreactions (irradiated at 350 nm) by ^{1}H NMR spectroscopy. The ratio of **3**/sensitizer was set to 1:3. Typical ^{1}H NMR spectral changes during the photolysis are shown in Figure S2 (Supporting Information). Figure 2 shows the time course of consumption of the starting dinaphthylethane **3** and formation of picene **2**. For **XT**-sensitized irradiation, neither significant consumption of dinaphthylethane **3** nor formation of picene **2** was observed. In the case of **DCA**-sensitized irradiation, 32% of the starting dinaphthylethane **3** was consumed, whereas a trace amount of picene **2** was observed (<3%) after 44 h of irradiation. It was found that, among the sensitized photolyses investigated, the photolysis of dinaphthylethane **3** in the presence of **9F** resulted in the highest yield of picene, with a yield of 25% accompanied by 53% consumption of dinaphthylethane **3**, after 44 h of irradiation. Prolonged irradiation was not effective for enhancing the yield (27% after 90 h). In the case of **BP** sensitization, conversion of dinaphthylethane **3** (61%) was the highest among the sensitized phtolyses investigated, however, the yield of picene **2** (11%) was lower than that for the **9F** sensitization. Therefore, **9F** was selected for use as the sensitizer in subsequent preparative studies of picene **2**.

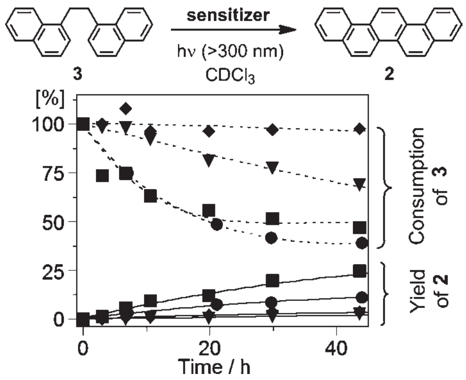


Figure 2. Time course of photolysis (350 nm, $CDCl_3$) of dinaphthylethane **3** sensitized with **9F** (■), **BP** (●), **XT** (♦), and **DCA** (▼). The solid and dotted lines show the yield of picene **2** and consumption of dinaphthylethane **3**, respectively.

In a small-scale preparation, a mixture of dinaphthylethane **3** (0.25 mmol) and **9F** (0.50 mmol) in $CHCl_3$ (50 mL) was irradiated with 350-nm fluorescent lamps for 38.5 h. After chromatographic separation, picene **2** was isolated in 14% yield. (Since 51% of dinaphthylethane **3** was recovered, the product yield based on consumed starting material was 28%.) Larger scale preparation was also conducted using typical experimental procedures outlined as follows. A solution of dinaphthylethane **3** (9.7 mmol) and **9F** (29 mmol) in $CHCl_3$ (450 mL) was irradiated with a 450-W high-pressure mercury arc lamp under N_2 atmosphere. After 48 h of irradiation, the solvent was removed under reduced pressure and the residue was washed with

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(3) Mitsuhashi, R.; Suzuki, Y.; Yamanari, Y.; Mitamura, H.; Kambe, T.; Ikeda, N.; Okamoto, H.; Fujiwara, A.; Yamaji, M.; Kawasaki, N.; Maniwa, Y.; Kubozono, Y. *Nature* **2010**, *464*, 76.

(4) For some reported picene syntheses, see: (a) Mallory, F. B.; Mallory, C. W. *Org. React.* **1984**, *30*, 1. (b) Harvey, R. G.; Pataki, J.; Cortez, C.; Di Raddo, P.; Yang, C. X. *J. Org. Chem.* **1991**, *56*, 1210. (c) Minuti, L.; Taticchi, A.; Gacs-Baitz, E.; Marrocchi, A. *Tetrahedron* **1998**, *54*, 10891. (d) Some, S.; Dutta, B.; Ray, J. K. *Tetrahedron Lett.* **2006**, *47*, 1221. (e) Nakano, Y.; Saito, M.; Nakamura, H. WO 2010016511 A1 20100211, 2010; *Chem. Abstr.* **2010**, *152*, 276730.

(5) Slocum, G. H.; Schuster, G. B. *J. Org. Chem.* **1984**, *49*, 2177.

$CHCl_3$ to afford picene **2** (15–20% yield based on the dinaphthylethane **3** used). It is worth noting that no appreciable impurity was detected using ^{1}H NMR spectroscopy in the *crude* product **2** obtained by the above workup procedure (Figure S3, Supporting Information). It can be concluded that the **9F**-sensitized photolysis of dinaphthylethane **3** provides a simple and convenient procedure for the synthesis of picene **2**. Higher purity samples of picene **2** suitable for use in the fabrication of organic electronic devices could be obtained by sublimation of the crude product under reduced pressure.[6]

Because the yield of picene **2** from the **9F**-sensitized photolysis of dinaphthylethane **3** was not affected by the amount of dissolved oxygen (data not shown), any contribution of the triplet state of **9F** to the formation of picene **2** can be excluded. In order to gain mechanistic insight into the photoinduced formation of picene, transient absorption spectra were measured for dinaphthylethane **3** in the presence of **9F** (Figure 3). An intense transient absorption band with the absorption maximum at 425 nm, assigned to triplet **9F**,[7] was seen upon 355-nm laser photolysis of **9F** in CCl_4. In contrast, in $CHCl_3$, the intensity of the triplet absorption of **9F** decreased compared to that in CCl_4, and the intensity was not affected by the amount of dinaphthylethane **3**. When the **9F**-sensitized photolysis of dinaphthylethane **3** was performed in CCl_4 as the solvent, only a trace amount of picene **2** was detected in the photolysate. These observations indicate the existence of a chemical interaction between the excited singlet state of **9F** and $CHCl_3$. Because picene formation unambiguously proceeds from dinaphthylethane **3** upon photosensitization with **9F** in $CHCl_3$, chemical intermediates generated from the interaction between the excited singlet state of **9F** and $CHCl_3$ may play a key role in promoting the pertinent cyclization.

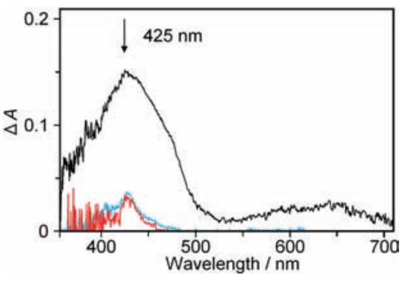
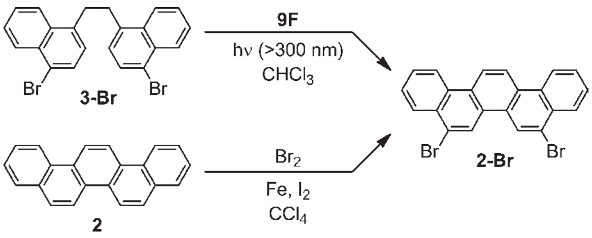


Figure 3. Transient absorption spectra obtained at 100 ns upon 355-nm laser pulsing in **9F** in CCl_4 (black line), and in the absence (blue line) and presence (red line) of dinaphthylethane **3** in $CHCl_3$.

A large number of functionalized aromatic hydrocarbons, namely pentacene-derived ones, have been synthesized with the aim of developing novel materials for organic electronic devices.[1] Trialkysilylethynyl functionalities have been used to modify both the electronic properties and the orientations of pentacene cores in the solid state.[8] In addition, sulfur-containing groups[9] and cyano gorups[10] have been used to enhance the stability of the pentacene core against exposure to air and light. For benzothienobenzothiophene-based organic FETs, long alkyl chains could be used to modify aggregation of the aromatic nuclei in the crystalline state.[11] It has recently been suggested that appropriately substituted picenes are also applicable to the active layer of organic FETs.[4e] Therefore, derivatization of picene **2** is ardently desired for elucidation of the electronic properties of picene-derived materials. However, systematic functionalization of the picene core has rarely been reported. We have found that functionalized picenes can be readily prepared in moderate to good yields by conventional substitution and cross-coupling reactions starting with brominated picene **2-Br** (Schemes 2 and 3).

Scheme 2. Preparation of Dibromopicene **2-Br**



Subjection of di(bromonaphthyl)ethane **3-Br** to the **9F**-sensitized photolysis yielded dibromopicene **2-Br** in a 25% yield. The dibromopicene **2-Br** could also be prepared by direct bromination of picene **2** (Scheme 2). The bromine atoms were replaced with CN groups using CuCN to afford **2-CN** in 70% yield. Palladium-catalyzed cross coupling of dibromopicene **2-Br** with thiophenol[12] produced **2-SPh** (53%). The Sonogashira reaction[13] using triisopropylsilylacetylene and Suzuki–Miyaura cross-coupling[14] using phenylboronic acid resulted in the formation of **2-TIPS** (86%) and **2-Ph** (26%), respectively. Alkyl substituents can be introduced into an aromatic nucleus by means of the Kumada–Tamao cross-coupling reaction.[15] Thus, dibromopicene **2-Br** was reacted with tridecylmagnesium bromide in the presence of a Pd catalyst to afford the alkyl-substituted picene, **2-C13** (69%). All of the new functionalized picenes obtained were characterized by NMR and IR spectroscopic analyses as well as mass spectrometry.

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(6) Okamoto, H.; Kubozono, Y.; Yamaji, M.; Goda, M. *Jpn. Kokai Tokkyo Koho* JP 2010143895, 2010; *Chem. Abstr*. **2010**, *153*, 115918.

(7) Carmichael, I.; Hug, G. L. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1.

(8) Payne, M. M.; Parkin, S. R.; Anthony, J. E.; Kuo, C.-C.; Jackson, T. N. *J. Am. Chem. Soc*. **2005**, *127*, 4986.

(9) Kaur, I.; Jia, W.; Kopreski, R. P.; Selvarasah, S.; Dokmeci, M. R.; Pramanik, C.; McGruer, N. E.; Miller, G. P. *J. Am. Chem. Soc*. **2008**, *130*, 16274.

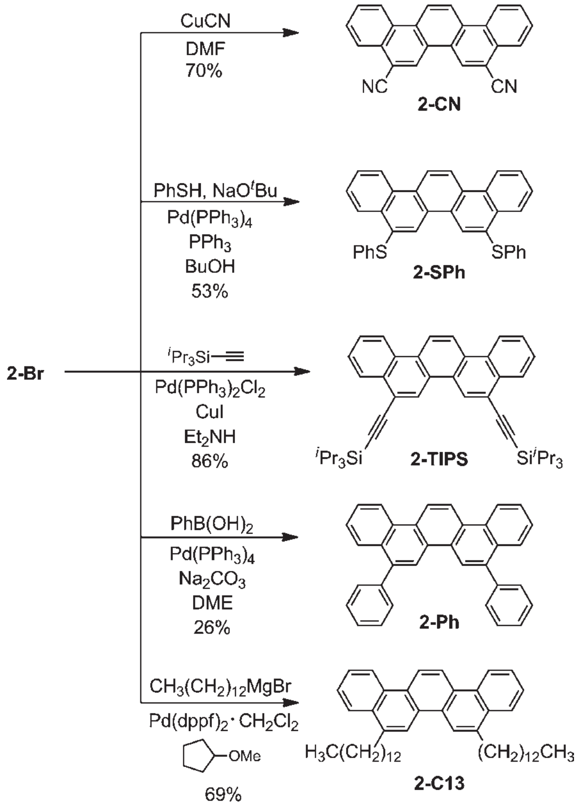
(10) Kuo, M.-Y.; Chen, H.-Y.; Chao, I. *Chem.—Eur. J*. **2007**, *13*, 4750.

(11) Ebata, H.; Izawa, T.; Miyazaki, E.; Takimiya, K.; Ikeda, M.; Kuwabara, H.; Yui, T. *J. Am. Chem. Soc*. **2007**, *129*, 15732.

(12) Migita, T.; Shimizu, T.; Asami, Y.; Shiobara, J.; Kato, Y.; Kosugi, M. *Bull. Chem. Soc. Jpn*. **1980**, *53*, 1385.

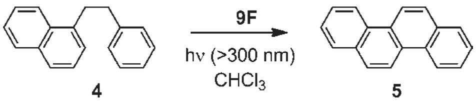
(13) Sonogashira, K. *J. Organomet. Chem*. **2002**, *653*, 46.

Scheme 3. Preparation of Functionalized Picenes



In summary, the present **9F**-sensitized photolysis of dinaphthylethane **3** provides a simple and convenient route to the facile synthesis of picene **2**. To the best of our knowledge, this is the first photochemical cyclization of ethylene-linked naphthalene chromophores to afford the picene framework **2**. In the **9F**-sensitized photolysis of naphthylphenylethane **4**, production of chrysene **5**—a lower phenacene—was confirmed although its yield was low (~3%, Scheme 4). Thus, the **9F**-sensitized ring-closure of 1,2-diaryl-substituted ethane would provide a novel and powerful strategy for construction of phenacene skeletons. Detailed photophysical studies are underway to clarify the photoreaction mechanisms. Various functionalized picenes could be systematically obtained by conventional substitution and cross-coupling reactions using dibromopicene **2-Br** as the precursor. Currently, the characteristics of the new picenes as organic electronics are under investigation.

Scheme 4. 9F-Sensitized Irradiation of Naphthylphenylethane **4**



Acknowledgment. Part of this work was performed under the Cooperative Research Program of the "Network Joint Research Center for Materials and Devices." H.O. and M.Y. are grateful for the financial support through Grants-in-Aid for Scientific Research (KAKENHI) from JSPS (Nos. 21550134 and 23350059). We are grateful to the SC-NMR Laboratory of Okayama University for the NMR spectral measurements. Mr. Takaaki Mikoshiba at Gunma University is acknowledged for his assistance in this work.

Supporting Information Available. Details of experimental procedures; ^{1}H and ^{13}C NMR spectra of the new compounds. This material is available free of charge via the Internet at http://pubs.acs.org

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(14) Suzuki, A. *Acc. Chem. Res.* **1982**, *15*, 178.

(15) Minato, A.; Tamao, K.; Hayashi, T.; Suzuki, K.; Kumada, M. *Tetrahedron Lett.* **1980**, *21*, 845.