# Formation of 4-Methylphenanthrenes in Palladium-Catalyzed Annulation of Diethyl 2,2′-Diiodo-4,4′-biphenyldicarboxylate with Internal Alkynes, Using Methyl Nitrobenzoates as the Methylating Agent

Ashis Baran Mandal, Gene-Hsiang Lee, Yi-Hung Liu, Shie-Ming Peng, and Man-kit Leung*

*Department of Chemistry, National Taiwan University, Taipei, Taiwan 106, Republic of China*

*Received July 9, 1999*

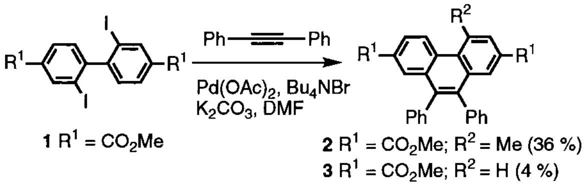
The reaction of diethyl 2,2′-diiodo-4,4′-biphenyldicarboxylate (**7**) with diarylacetylenes in the presence of 3,5-$(NO_2)_2C_6H_3CO_2Me$ (MeDNB) or 4-$(NO_2)C_6H_4CO_2Me$ (MePNB), $Pd(OAc)_2$ (10 mol %), $K_2CO_3$, and $Bu_4NBr$, in DMF at 100 °C, gives 4-methyl-9,10-diaryl-2,7-phenanthrenedicarboxylic acid diethyl esters in good yields. The methyl group at position 4 originates from the electron-deficient methyl nitrobenzoates. High regioselectivity for the annulation of **7** with nonsymmetrical diarylalkynes was observed with the selectivity controlled mainly by electronic factors rather than by steric factors. A competitive kinetic isotope study was carried out using a 1:1 mixture of MePNB and MePNB-$d_3$ in the annulation reaction of **7** which gave 4-methyl- and 4-(methyl-$d_3$)phenanthrene in a 67:33 ratio, leading to an apparent value of $k_H/k_D = 1.26$. Possible mechanisms for the methyl transferring process are discussed.

## Introduction

Palladium-catalyzed reactions of aryl iodides with alkynes are quite interesting because of their potential for one-pot synthesis of polycyclic aromatic compounds.[1,2] For example, the annulation of 2-iodobiphenyls with internal alkynes was shown to give 9,10-disubstituted phenanthrenes.[2a,j] In other cases, 2,2′-diiodobiphenyls underwent palladium-catalyzed phenylethynylation with 2 mol of phenylacetylene to yield 3-(fluoren-9-ylidene)-1,3-diphenylpropynes.[2m] Herein, we disclose the unexpected results obtained in the annulation reaction of dimethyl 2,2′-diiodo-4,4′-biphenyldicarboxylate (**1**) with internal alkynes.

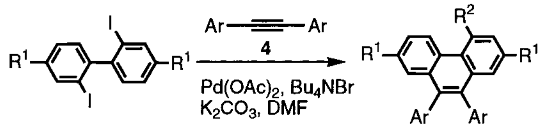
## Results and Discussion

When the reaction of **1** with 2 equiv of diphenylacetylene was carried out in the presence of $Pd(OAc)_2$ (10 mol %), $K_2CO_3$, and $Bu_4NBr$ in DMF at 100 °C, we obtained two fluorescent compounds which were characterized as 4-methyl-9,10-diphenyl-2,7-phenanthrenedicarboxylic acid dimethyl ester (**2**) (36%) and 9,10-diphenyl-2,7-phenanthrenedicarboxylic acid dimethyl ester (**3**) (4%), respectively. The structure of **2** was further confirmed by X-ray crystallographic analysis. A similar reaction of **1** with **4** also gave a mixture of two compounds, **5** and **6** in 32% yield (15:1). These intriguing observations led us to investigate the mechanism of this methyl transferring reaction.



**1** $R^1 = CO_2Me$

**2** $R^1 = CO_2Me$; $R^2 = Me$ (36 %)
**3** $R^1 = CO_2Me$; $R^2 = H$ (4 %)



**1** $R^1 = CO_2Me$

**5** $R^1 = CO_2Me$; $R^2 = Me$;
$Ar = C_6H_4CO_2Me$ (30 %)
**6** $R^1 = CO_2Me$; $R^2 = H$;
$Ar = C_6H_4CO_2Me$ (2 %)

To allocate the methyl source in this reaction, we carried out independent experiments under three different conditions: (1) diphenylacetylene, **1**, $PdCl_2$ (10 mol %), $Ph_3P$, $K_2CO_3$, $Bu_4NBr$, and DMF; (2) diphenylacetylene, **1**, $Pd(OAc)_2$ (10 mol %), $K_2CO_3$, $Bu_4NBr$, and DMF-$d_7$; and (3) diphenylacetylene, $(EtO_2CC_6H_3I)_2$ (**7**), $Pd(OAc)_2$ (10 mol %), $K_2CO_3$, $Bu_4NBr$, and DMF. Under the first two conditions, the reaction yielded the same products in comparable ratios and yield percentages (Table 1, entries 1 and 2). These observations clearly ruled out the possibility that methyl was transferring from either the decomposition of the acetate ligand or from DMF. On the other hand, the replacement of methyl ester **1** with ethyl ester **7** in the third experiment (entry 3) strongly retarded the reaction. After 8 days of reaction, only nonmethylated phenanthrene (**8**) was isolated, in low yield (<10%), along

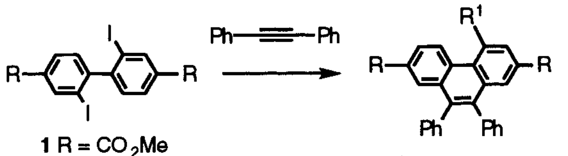
---

(1) For a general reviews, see: (a) Tsuji, J. *Palladium Reagents and Catalysts;* Wiley: New York, 1995. (b) Sonogashira, K. In *Comprehensive Organic Synthesis;* Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 3, p 521. (c) Rossi, R.; Carpita, A.; Bellina, F. *Org. Prep. Proced. Int.* **1995**, 129.

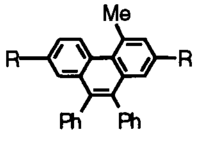
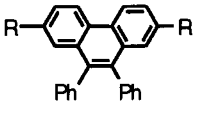
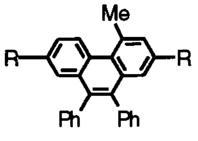
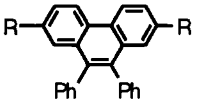
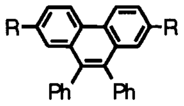
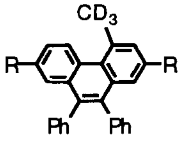
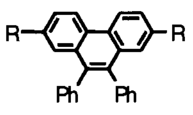
(2) For current examples, see: (a) Larock, R. C.; Doty, M. J.; Tian, Q.; Zenner, J. M. *J. Org. Chem.* **1997**, *62*, 7536. (b) Larock, R. C.; Yum, E. K.; Doty, M. J.; Sham, K. K. C. *J. Org. Chem.* **1995**, *60*, 3270. (c) Larock, R. C.; Doty, M. J.; Cacchi, S. *J. Org. Chem.* **1993**, *58*, 4579. (d) Spencer, J.; Pfeffer, M.; DeCian, A.; Fischer, J. *J. Org. Chem.* **1995**, *60*, 1005. (e) Spencer, J.; Pfeffer, M.; Kyritsakas, N.; Fischer, J. *Organometallics* **1995**, *14*, 2214. (f) Pfeffer, M.; Rotteveel, M. A.; Borgne, G. L.; Fischer, J. *J. Org. Chem.* **1992**, *57*, 2147. (g) Beydoun, N.; Pfeffer, M. *Synthesis* **1990**, 729. (h) Tao, W.; Silverberg, L. J.; Rheingold, A. L.; Heck, R. F. *Organometallics* **1989**, *8*, 2550. (i) Wu, G.; Rheingold, A. L.; Geib, S. J.; Heck, R. F. *Organometallics* **1987**, *6*, 1941. (j) Wu, G.; Rheingold, A. L.; Heck, R. F. *Organometallics* **1987**, *6*, 2386. (k) Dyker, G.; Kellner, A. *Tetrahedron Lett.* **1994**, *35*, 7633. (l) Dyker, G. *J. Org. Chem.* **1993**, *58*, 234. (m) Dougherty, T. K.; Lau, K. S. Y.; Hedberg, F. L. *J. Org. Chem.* **1983**, *48*, 5273.

10.1021/jo991100u CCC: $19.00

**Table 1. Palladium-Catalyzed Annulation Reaction of Dialkyl 2,2′-Diiodo-4,4′-biphenyldicarboxylate with Diphenyl Acetylene under Various Conditions at 100 °C**



**1** $R = CO_2Me$
**7** $R = CO_2Et$
**9** $R = CO_2CD_3$

| Entry | Products (yield %)$^e$ |
|---|---|
| 1$^a$ |  **2** $R = CO_2Me$ (38)<br> **3** $R = CO_2Me$ (4) |
| 2$^b$ |  **2** $R = CO_2Me$ (28)<br> **3** $R = CO_2Me$ (7) |
| 3$^c$ |  **8** $R = CO_2Et$ (9) |
| 4$^d$ |  **10** $R = CO_2CD_3$ (13)<br> **11** $R = CO_2CD_3$ (2) |

[a] **1** ($R = CO_2Me$), $PdCl_2$ (10 mol %), $Ph_3P$, DMF, $K_2CO_3$, $Bu_4NBr$, 3 days. [b] **1** ($R = CO_2Me$), $Pd(OAc)_2$ (10 mol %), $K_2CO_3$, $Bu_4NBr$, DMF-$d_7$, 3 days. [c] **7** ($R = CO_2Et$), $Pd(OAc)_2$ (10 mol %), $K_2CO_3$, $Bu_4NBr$, DMF, 8 days. [d] **9** ($R = CO_2CD_3$), $Pd(OAc)_2$ (10 mol %), $K_2CO_3$, $Bu_4NBr$, DMF, 5 days. [e] In entries 1, 2, and 4, the starting diiodo compounds were almost consumed. In entry 3, ~80% of **7** was recovered.

with the recovery of, primarily, the starting materials (80%). All of these results indicated that the methyl group originated from **1**. Direct proof was further obtained from the annulation reaction of $(CD_3O_2CC_6H_3I)_2$ (**9**) with diphenylacetylene, which afforded (methyl-$d_3$)phenanthrene (**10**) as the major product (13%, Table 1 entry 4).

In order to improve the potential of this reaction, and to search for an efficient methyl source, the annulation reaction of **7** with diphenylacetylene was examined using a series of readily available methyl carboxylates as the methyl transferring agents (Table 2). Among the methyl carboxylates used, including methyl benzoate, methyl *p*-methoxybenzoate, dimethyl isophthalate, methyl *p*-nitrobenzoate (MePNB), and methyl 3,5-dinitrobenzoate (MeDNB), only the electron-deficient esters MePNB and MeDNB could transfer the methyl group effectively. The yield of **12** was improved dramatically, to 63%, by using 4 equiv of MeDNB as the methyl transferring agent. In another example, shown in entry 8, using MePNB as the reagent, the yield of **12** was improved to 48%.

In contrast with earlier observations in other related systems,[2b−e,g,k] high regioselectivity for the annulation of **7** with nonsymmetrical diarylalkynes (Table 2, entries 9 and 10) was observed, giving only single regioisomers **13** (58%) and **14** (49%), respectively. The structural assignments of **13** and **14** were confirmed by proton−proton 2D-COSY and 2D-NOESY experiments. Furthermore, the unequivocal regiochemical assignment of **14** was established by X-ray crystallographic analysis. Because the distal substituents at the para position of the diphenylacetylene should have little steric influence on the selectivity, electronic factors may play an important role in the regiochemical outcome.

To probe the details of the reaction mechanism, a competitive kinetic isotope study was carried out, using a 1:1 mixture of MePNB and MePNB-$d_3$ in the annulation reaction of **7**, which gave 4-methyl- and 4-(methyl-$d_3$)phenanthrene in a 67:33 ratio, leading to an apparent value of $k_H/k_D = 1.26$.[3] This value falls into a typical region of the secondary kinetic isotope effect, indicating that the methyl transferring process may play an important role in the rate-determining step. This result also explains the low yield of **10** (Table 1, entry 4) in the previous experiment.

Although the yield of the annulation was slightly improved when $Bu_4NI$ was used, instead of $Bu_4NBr$ (Table 2, entries 5 and 6), the reaction rate was maintained at the same order of magnitude. However, when $Bu_4NBr$ (Table 2, entry 7) was replaced by $Bu_4NOT$, the reaction became extremely sluggish, and less than 10% yield was obtained after a reaction time of 3 days. On the other hand, direct use of MeI (4 equiv) as the methyl transferring agent gave **12** in only very low yield (entry 11).

To explain the above observations, a possible mechanism for the methyl transferring reaction is proposed in Scheme 1. Halide ions from either $Bu_4NBr$ or $Bu_4NI$ may act as nucleophiles, provoking an $S_N2$-type demethylation of electron-deficient methyl benzoates, thereby releasing halomethane slowly into the reaction mixture.[4] Isolation of 3,5-dinitrobenzoic acid from the product mixture further supports this argument.[5] Oxidative addition of halomethanes to Pd(II) intermediate **17**[2m] would lead to Pd(IV) intermediate **18**, which may facilitate the aryl−methyl coupling reaction to give **19**. Indeed, formation of Pd(IV) complexes and aryl−alkyl coupling through Pd(IV) intermediates have recently been reported.[6] Intermediate **19** would then undergo the palladium-

---

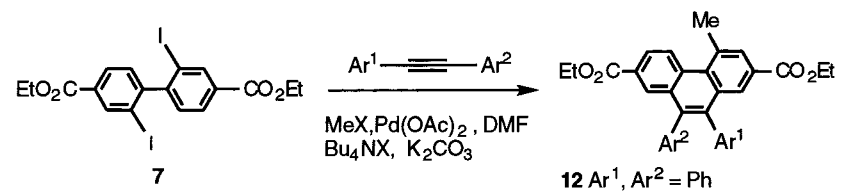
(3) Because the details of the mechanism have not been clearly established, only the apparent value of $k_H/k_D$ (the product ratio of **12** and **12**-$d_3$)$^{1/3}$ was reported, with the assumption that the relative reaction rate is directly reflected in the product ratio. For reference, see: Maskill, H. *The Physical Basis of Organic Chemistry*; Oxford University Press: Oxford, 1989; pp 367−404.

(4) Elsinger, F.; Schreiber, J.; Eschenmoser, A. *Helv. Chim. Acta* **1960**, *43*, 113.

(5) 3,5-Dinitrobenzoic acid was isolated from the solid residue of the reaction mixture that contained potassium 3,5-dinitrobenzoate. As in Table 2, entry 9, ~80% of 3,5-dinitrobenzoic acid could be isolated after chromatography. The product was identified by $^1H$ NMR in DMSO-$d_6$.

(6) (a) Canty, A. J.; van Koten, G. *Acc. Chem. Res.* **1995**, *28*, 406. (b) Catellani, M.; Cugini, F. *Tetrahedron* **1999**, *55*, 6595. (c) Catellani, M.; Frignani, F.; Rangoni, A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 119. (d) Catellani, M.; Fagnola, M. C. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2421. (e) Bocelli, G.; Catellani, M.; Ghelli, S. *J. Organomet. Chem.* **1993**, *458*, C12.

**Table 2. Preparation of 4-Methylphenanthrene 12–14 by Reaction of 7 with Diarylacetylenes Using Readily Available Methyl Carboxylates as the Methyl Transferring Agents**

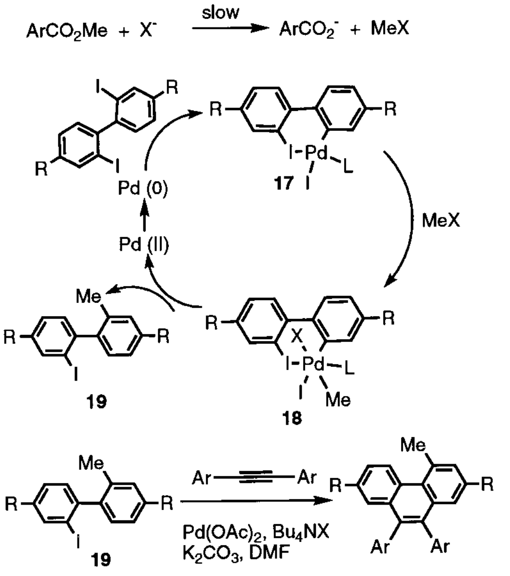


**7**

**12** $Ar^1, Ar^2 = Ph$
**13** $Ar^1 = C_6H_4CO_2Et, Ar^2 = Ph$
**14** $Ar^1 = Ph, Ar^2 = C_6H_4OMe$

| entry | $Ar^1/Ar^2$ | $Bu_4NX$ (equiv) | MeX | equiv | product (yield %) |
|---|---|---|---|---|---|
| 1 | Ph/Ph | $Bu_4NBr$ (2) | $PhCO_2Me$ | 1 | **12** (<5) |
| 2 | Ph/Ph | $Bu_4NBr$ (2) | $4\text{-}MeOC_6H_4CO_2Me$ | 1 | **12** (<5) |
| 3 | Ph/Ph | $Bu_4NBr$ (2) | $1,3\text{-}C_6H_4(CO_2Me)_2$ | 1 | **12** (<5) |
| 4 | Ph/Ph | $Bu_4NBr$ (2) | $3,5\text{-}(NO_2)_2C_6H_3CO_2Me$ | 1 | **12** (14) |
| | | | | 2 | **12** (36) |
| | | | | 4 | **12** (63) |
| 5 | Ph/Ph | $Bu_4NBr/Bu_4NI$ (2):(0.5) | $3,5\text{-}(NO_2)_2C_6H_3CO_2Me$ | 4 | **12** (74) |
| 6 | Ph/Ph | $Bu_4NI$ (2) | $3,5\text{-}(NO_2)_2C_6H_3CO_2Me$ | 4 | **12** (71) |
| 7 | Ph/Ph | $Bu_4NOTs$ (2) | $3,5\text{-}(NO_2)_2C_6H_3CO_2Me$ | 4 | **12** (8) |
| 8 | Ph/Ph | $Bu_4NBr$ (2) | $4\text{-}(NO_2)C_6H_4CO_2Me$ | 4 | **12** (48) |
| 9 | $p\text{-}C_6H_4CO_2Et/Ph$ (**15**) | $Bu_4NBr$ (2) | $3,5\text{-}(NO_2)_2C_6H_3CO_2Me$ | 4 | **13** (58) |
| 10 | $Ph/p\text{-}C_6H_4OMe$ (**16**) | $Bu_4NBr$ (2) | $3,5\text{-}(NO_2)_2C_6H_3CO_2Me$ | 4 | **14** (49) |
| 11 | Ph/Ph | $Bu_4NBr$ (2) | MeI | 4 | **12** (<5) |

**Scheme 1**



catalyzed annulation to afford the corresponding 4-methylphenanthrene. This mechanism explains the secondary kinetic isotope effects as well as the substituent effects of the methyl benzoate. One important aspect is the slow release of the halomethane to the reaction mixture, which keeps the halomethane at low concentration during the course of the reaction.[9] Competitive homocoupling[8,9b] of MeI may occur at high concentration in the direct addition experiment (Table 2, entry 11), leading to a fast consumption of MeI in the early stage of the reaction and therefore prohibiting the methylation of **17** and the formation of phenanthrene. Although the above suggestion could reasonably explain the observations, the formation of $MePdXL_2$ from MeX and Pd(0)[9,10] could also yield methylate **17** through a bimolecular reaction without forming a Pd(IV) complex. Moreover, the possibility of direct methyl transfer from methyl carboxylate to Pd(0) or Pd(II) intermediate **17** could not be eliminated. Another point refers to the role of the ammonium halides, which might be important not only as a source of the halide ions but also for the formation of anionic palladium complexes. All of these possibilities need to be clarified.

The mechanism for the formation of nonmethylated phenanthrenes **3**, **8**, and **11** in the reaction is unclear. Nevertheless, this reaction pathway was suppressed in the presence of MePNB or MeDNB, implying a competition between two reaction pathways. Moreover, annulation of **7** in DMF-$d_7$ in the absence of a methyl transferring agent still provides nondeuterated **8** as the product, indicating that the proton arises from a source other than DMF. Although we have insufficient evidence, we suggest that moisture present in the reaction mixture may be acting as a major proton source for this reaction.

## Conclusion

In summary, reactions of diethyl 2,2′-diiodo-4,4′-biphenyldicarboxylate with internal diarylalkynes and methyl nitrobenzoates provide a new approach for the synthesis of 4-methylphenanthrenes. Further support to the proposed mechanism is now under investigation.

## Experimental Section

**General and Materials.** Palladium(II) acetate, ($Pd(OAc)_2$), tetrabutylammonium iodide ($Bu_4NI$), tetrabutylammonium

---

(7) It has been known that the slow addition of alkyl halides would benefit the aryl–alkyl coupling. For reference, see 6b.

(8) Heck, R. F. *Palladium Reagents in Organic Synthesis;* Academic Press: New York, 1985; p 179. (b) Becker, Y.; Stille, J. K. *J. Am. Chem. Soc.* **1978**, *100*, 838.

(9) (a) Heck, R. F. *Acc. Chem. Res.* **1979**, *12*, 146. (b) Stille, J. K.; Lau, K. S. Y. *Acc. Chem. Res.* **1977**, *10*, 434. (c) Kramer, A. V.; Labinger, J. A.; Bradley, J. S.; Osborn, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 7145. (d) Kramer, A. V.; Osborn, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 7832. (e) Fitton, P.; Johnson, M. P.; Mckeon, J. E. *J. Chem. Soc., Chem. Commun.* **1968**, 6. (f) Fitton, P.; Mckeon, J. E.; Ream, B. C. *J. Chem. Soc., Chem. Commun.* **1969**, 370. (g) Mizoroki, T.; Mori, K.; Ozaki, A. *Bull. Chem. Soc. Jpn.* **1972**, *44*, 581.

(10) (a) Ozawa, F.; Ito, T.; Nakamura, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1868. (b) Negishi, E. *Acc. Chem. Res.* **1982**, *15*, 340.

bromide ($Bu_4NBr$), tetrabutylammonium tosylate (TBAOTs), potassium carbonate, DMF, and DMF-$d_7$ were obtained commercially (Aldrich, Janssan, Tokyo Kasei). $Pd(OAc)_2$ was used as received. $Bu_4NI$ and $Bu_4NBr$ was recrystallized from acetone and dried under vacuum before use. $K_2CO_3$ was dried under vacuum at 110 °C for 24 h. DMF was dried over molecular sieves (4A). Dialkyl 2,2′-diiodo-4,4′-biphenyldicarboxylates **1** and **7**,[11] dimethyl 4,4′-diphenylacetylenedicarboxylate (**4**),[12] ethyl 4-phenylethynylbenzoate (**15**),[12] and 4-phenylethynylanisole (**16**)[13] were prepared according to the literature procedures. The methyl esters used as the methyl transferring agents in this paper were prepared from the corresponding commercially available carboxylic acids, according to the literature procedures.[14] All the palladium-catalyzed reactions were run under a dry argon atmosphere, unless otherwise noted. $^1H$ and $^{13}C$ NMR were recorded in $CDCl_3$, and chemical shifts are reported in ppm relative to $CHCl_3$ ($\delta$ 7.24 ppm for $^1H$ and 77.0 ppm for $^{13}C$). The melting points are uncorrected.

**Typical Procedure A for the Preparation of 2 and 5.** A mixture of dimethyl 2,2′-diiodo-4,4′-biphenyldicarboxylate (**1**) (1 mmol), diarylacetylene (2 mmol), $Pd(OAc)_2$ (10 mol %), $K_2CO_3$ (8 mmol), $Bu_4NBr$ (2 mmol), and DMF (10 mL) was reacted at 100 °C for 3 days under argon. The reaction mixture was cooled, the solid residue was filtered off, and DMF was removed under vacuum. The crude oily residue was diluted with $CH_2Cl_2$ (20 mL), washed with water (10 mL), dried over anhydrous $MgSO_4$, purified by column chromatography over silica gel, and recrystallized.

**4-Methyl-9,10-diphenyl-2,7-phenanthrenedicarboxylic Acid Dimethyl Ester (2).** The reaction of **1** (522 mg, 1 mmol) with diphenylacetylene (356 mg, 2 mmol) gave a crude product of **2**. After preliminary purification through chromatography on silica gel, using $CH_2Cl_2$/hexanes (1:1) as the eluent, recrystallization from $CHCl_3$/hexanes (1:1), gave essentially pure **2** (166 mg, 36%) as slightly yellowish crystals: mp 318−319 °C; IR cm$^{-1}$ (KBr) 1733 (C═O); $^1H$ NMR (300 MHz, $CDCl_3$, $\delta$) 3.22 (s, 3 H), 3.84 (s, 3 H), 3.85 (s, 3 H), 7.08−7.12 (m, 10 H), 8.14 (s, 2 H), 8.21 (dd, $J = 8.8$, 1.8 Hz, 1 H), 8.29 (d, $J = 1.8$ Hz, 1 H), 8.95 (d, $J = 9$ Hz, 1 H); $^{13}C$ NMR (100 MHz, $CDCl_3$, $\delta$) 27.38, 52.23, 125.09, 126.85, 126.87, 127.63, 127.75, 127.77, 127.94, 128.00, 128.14, 129.56, 130.79, 130.82, 130.85, 132.79, 133.45, 133.56, 134.05, 135.97, 138.29, 138.51, 138.94, 166.93, 166.95; MS (70 eV) 460 (M$^+$). Anal. Calcd for $C_{31}H_{24}O_4$: C, 80.84; H, 5.26. Found: C, 80.29; H, 5.18.

**4-Methyl-9,10-di(4-carbomethoxyphenyl)-2,7-phenanthrenedicarboxylic Acid Dimethyl Ester (5).** The reaction of **1** (522 mg, 1 mmol) with 4,4′-diphenylacetylenedicarboxylic acid dimethyl ester (**4**) (588 mg, 2 mmol) gave a crude mixture with **5** as the major product. After preliminary purification by chromatography on silica gel, using $CH_2Cl_2$/hexanes (9:1) as the eluent, recrystallization from $CHCl_3$/hexanes (1:1) gave essentially pure **5** (173 mg, 30%) as bright yellowish crystals: mp 264−265 °C; IR cm$^{-1}$ (KBr) 1727 (C═O); $^1H$ NMR (200 MHz, $CDCl_3$, $\delta$) 3.22 (s, 3 H), 3.84 (s, 3 H), 3.85 (s, 3 H), 3.90 (s, 6 H), 7.18 (d, $J = 8$ Hz, 2 H), 7.19 (d, $J = 8$ Hz, 2 H), 7.92 (d, $J = 8$ Hz, 4 H), 8.02 (d, $J = 1.8$ Hz, 1 H), 8.17 (s, 2 H), 8.24 (dd, $J = 8$, 1.8 Hz, 1 H), 8.97 (d, $J = 8$ Hz, 1 H); $^{13}C$ NMR (100 MHz, $CDCl_3$, $\delta$) 27.27, 52.06, 52.22, 125.55, 127.58, 127.85, 127.99, 128.21, 128.83, 128.85, 129.00, 129.19, 129.22, 130.77, 130.81, 131.24, 132.62, 132.75, 133.11, 133.44, 136.17, 137.16, 137.83, 143.10, 143.54, 166.50, 166.53, 166.69; MS−FAB 576 (M$^+$). Anal. Calcd for $C_{35}H_{28}O_8$: C, 72.89; H, 4.90. Found: C, 72.50; H, 4.68.

**9,10-Diphenyl-2,7-phenanthrenedicarboxylic Acid Diethyl Ester (8).** The reaction of **7** (550 mg, 1 mmol) with diphenylacetylene (178 mg, 1 mmol) in the presence of $Pd(OAc)_2$ (22 mg, 10 mol %), $Bu_4NBr$ (644 mg, 2 mmol), and $K_2CO_3$ (1.1 gm, 8 mmol) in DMF (10 mL) at 100 °C for 8 days under argon gave **8** (43 mg, 9%) as colorless crystals: mp 249−250 °C; IR cm$^{-1}$ (KBr) 1718 (C═O); $^1H$ NMR (200 MHz, $CDCl_3$, $\delta$) 1.32 (t, $J = 7.2$ Hz, 6 H), 4.27−4.38 (q, $J = 7.2$ Hz, 4 H), 7.10−7.25 (m, 10 H), 8.23−8.31 (m, 4 H), 8.84 (d, $J = 8.6$ Hz, 2 H); $^{13}C$ NMR (100 MHz, $CDCl_3$, $\delta$) 14.20, 61.10, 123.33, 126.45, 126.93, 127.75, 129.24, 130.12, 130.90, 132.27, 132.32, 138.36, 138.41, 166.44; MS−FAB 474 (M$^+$). Anal. Calcd for $C_{32}H_{26}O_4$: C, 80.99; H, 5.52. Found: C, 81.15; H, 5.32.

**4-(Methyl-$d_3$)-9,10-diphenyl-2,7-phenanthrenedicarboxylic Acid Di(methyl-$d_3$) Ester (10).** The reaction of **9** (528 mg, 1 mmol) with diphenylacetylene (178 mg, 1 mmol) in the presence of $Pd(OAc)_2$ (22 mg, 10 mol %), $Bu_4NBr$ (644 mg, 2 mmol), and $K_2CO_3$ (1.1 gm, 8 mmol) in DMF (10 mL) occurred at 100 °C for 3 days under argon. The reaction was performed according to procedure A. After preliminary purification through chromatography on silica gel, using $CH_2Cl_2$/hexanes (1:1) as the eluent, recrystallization from $CHCl_3$ gave compound **10** (61 mg, 13%) as light brown crystals: mp 307−308 °C; IR cm$^{-1}$ (KBr) 1729 (C═O); $^1H$ NMR (200 MHz, $CDCl_3$, $\delta$) 7.06−7.12 (m, 4 H), 7.19−7.25 (m, 6 H), 8.13−8.15 (m, 2 H), 8.18 (d, $J = 2$ Hz, 1 H), 8.23 (d, $J = 2$ Hz, 1 H), 8.29 (d, $J = 2$ Hz, 1 H), 8.94 (d, $J = 8$ Hz, 1 H); $^{13}C$ NMR (100 MHz, $CDCl_3$, $\delta$) 125.12, 126.86, 126.88, 127.70, 127.75, 127.78, 127.90, 128.07, 128.18, 129.59, 130.80, 130.85, 130.88, 132.83, 133.50, 133.59, 134.08, 135.86, 138.32, 138.55, 138.97, 138.99, 166.95, 166.98; MS−FAB 469 (M$^+$); HRMS−FAB calcd for $C_{31}{}^1H_{15}{}^2H_9O_4$ 469.2239, found 469.2264.

**Typical Procedure B for the Preparation of 12−14.** A mixture of diethyl-2,2′-diiodo-4,4′-biphenyldicarboxylate (1 mmol), diarylacetylene (1 mmol), $Pd(OAc)_2$ (10 mol %), $K_2CO_3$ (8 mmol), $Bu_4NBr$ or $Bu_4NI$ (2 mmol), 3,5-dinitromethylbenzoate (4 mmol), and DMF (10 mL) was reacted at 100 °C for 3 days under argon. The reaction mixture was cooled, the solid residue was filtered off, and DMF was removed under vacuum. The crude oily residue was diluted with $CH_2Cl_2$ (20 mL), washed with water (10 mL), dried over anhydrous $MgSO_4$, and purified by column chromatography over silica gel.

**4-Methyl-9,10-diphenyl-2,7-phenanthrenedicarboxylic Acid Diethyl Ester (12).** The reaction of **7** (550 mg, 1 mmol) with diphenylacetylene (178 mg, 1 mmol) in the presence of 3,5-dinitromethylbenzoate (904 mg, 4 mmol), $Pd(OAc)_2$ (22 mg, 10 mol %), $K_2CO_3$ (1.1 gm, 8 mmol), and $Bu_4NBr$ (644 mg, 2 mmol) in DMF (10 mL) gave **12** (308 mg, 63%) as light brown crystals: mp 151−152 °C; IR cm$^{-1}$ (KBr) 1719 (C═O); $^1H$ NMR (300 MHz, $CDCl_3$, $\delta$) 1.28−1.34 (m, 6 H), 3.22 (s, 3 H), 4.28−4.36 (m, 4 H), 7.09−7.26 (m, 10 H), 8.13 (s, 1 H), 8.16 (s, 1 H), 8.20 (dd, $J = 9$, 2 Hz, 1 H), 8.31 (d, $J = 2$ Hz, 1 H), 8.95 (d, $J = 9$ Hz, 1 H); $^{13}C$ NMR (100 MHz, $CDCl_3$, $\delta$) 14.14, 27.31, 60.97, 124.94, 126.77, 126.81, 127.66, 127.69, 127.80, 127.88, 128.19, 128.24, 129.58, 130.64, 130.81, 130.85, 132.65, 133.36, 133.51, 134.00, 135.83, 138.18, 138.52, 138.84, 138.96, 166.33, 166.35; MS−FAB 488 (M$^+$). Anal. Calcd for $C_{33}H_{28}O_4$: C, 81.12; H, 5.77. Found: C, 80.82; H, 5.58.

**4-Methyl-9-phenyl-10-(4-carbethoxyphenyl)-2,7-phenanthrenedicarboxylic Acid Diethyl Ester (13).** The reaction of **7** (550 mg, 1 mmol) with **15** (250 mg, 1 mmol) gave **13** (325 mg, 58%) as yellow crystals: mp 172−173 °C; IR cm$^{-1}$ (KBr) 1718 (C═O); $^1H$ NMR (300 MHz, $CDCl_3$, $\delta$) 1.28−1.40 (m, 9 H), 3.22 (s, 3 H), 4.27−4.38 (m, 6 H), 7.09 (d, $J = 7.8$ Hz, 2 H), 7.18−7.23 (m, 5 H), 7.92 (d, $J = 9$ Hz, 2 H), 8.05 (d, $J = 1.5$ Hz, 1 H), 8.14 (d, $J = 1.5$ Hz, 1 H), 8.22 (dd, $J = 9$, 1.8 Hz, 1 H), 8.29 (d, $J = 1.8$ Hz, 1 H), 8.96 (d, $J = 9$ Hz, 1 H); $^{13}C$ NMR (100 MHz, $CDCl_3$, $\delta$) 14.15, 14.21, 14.27, 27.36, 60.91, 61.07, 61.10, 125.26, 127.12, 127.75, 127.85, 127.90, 128.07, 128.39, 128.83, 129.01, 129.63, 130.69, 130.84, 130.97, 132.66, 133.36, 133.41, 133.48, 136.03, 137.79, 138.03, 138.25, 144.06, 166.25, 166.28, 166.44; MS−FAB 560 (M$^+$). Anal. Calcd for $C_{36}H_{32}O_6$: C, 77.12; H, 5.75. Found: C, 76.43; H, 5.55.

---

[11] (a) Kwong, C.-Y.; Chan, T.-L.; Chow, H.-F.; Lin, S.-C.; Leung, M.-k. *J. Chin. Chem. Soc.* **1997**, *44*, 211. (b) Hanson, M. P.; Marvel, C. S. *J. Polym. Sci., Polym. Lett. Ed.* **1978**, *16*, 653. (c) Lin, S. C.; Marvel, C. S. *J. Polym. Sci., Part A: Polym. Chem.* **1979**, *17*, 2337.

[12] (a) Rudenko, A. P.; Vasil'ev, A. V. *Russ. J. Org. Chem.* **1995**, *31*, 1360. (b) Beletskaya, I. P. *Pure Appl. Chem.* **1997**, *69*, 471.

[13] Al-Hassan, M. I. *J. Organomet. Chem.* **1990**, *395*, 227.

[14] *Vogel's Textbook of Practical Organic Chemistry*, 5th ed.; Furniss, B. S., Hannaford, A. J., Smith, P. W. G., Tatchell, A. R., Eds.; Longman: Essex, 1989; p 1077.

**4-Methyl-10-phenyl-9-(4-methoxyphenyl)-2,7-phenanthrenedicarboxylic Acid Diethyl Ester (14).** The reaction of **7** (550 mg, 1 mmol) with **16** (208 mg, 1 mmol) gave **14** (255 mg, 49%) as light yellow crystals: mp 138−139 °C; IR cm$^{-1}$ (KBr) 1780 (C=O); $^1$H NMR (400 MHz, CDCl$_3$, $\delta$) 1.29−1.36 (m, 6 H), 3.21 (s, 3 H), 3.77 (s, 3 H), 4.28−4.37 (m, 4 H), 6.77 (d, $J$ = 8 Hz, 2 H), 7.01 (d, $J$ = 8 Hz, 2 H), 7.08−7.11 (d, $J$ = 8 Hz, 2 H), 7.20−7.27 (m, 3 H), 8.12 (s, 1 H), 8.14 (s, 1 H), 8.20 (dd, $J$ = 8, 2 Hz, 1 H), 8.36 (d, $J$ = 2 Hz, 1 H), 8.93 (d, $J$ = 8 Hz, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$, $\delta$) 14.17, 14.24, 27.26, 55.15, 60.95, 60.98, 113.40, 124.96, 126.78, 127.76, 127.85, 128.11, 128.28, 128.48, 129.76, 130.63, 130.92, 130.98, 132.02, 132.75, 133.56, 134.07, 134.26, 135.82, 138.02, 139.25, 139.35, 158.46, 166.45, 166.48; MS−FAB 518 (M$^+$); HRMS−FAB calcd for $C_{34}H_{30}O_5$ 518.2093, found 518.2129.

**Preparation of Single Crystals of 4-Methyl-9,10-diphenyl-2,7-phenanthrenedicarboxylic Acid Dimethyl Ester (2).** The slow evaporation of the solvent from a solution of **2** in CHCl$_3$ affords slightly yellowish crystals that are suitable for X-ray crystallographic analysis. For the structural details of **2**, one can refer to the ORTEP drawing and the data listed in the Supporting Information.

**Preparation of Single Crystals of 4-Methyl-10-phenyl-9-(4-methoxyphenyl)-2,7-phenanthrenedicarboxylic Acid Diethyl Ester (14).** The slow evaporation of the solvent from a solution of **2** in EtOAc affords light yellowish crystals that are suitable for X-ray crystallographic analysis. For the structural details of **2**, one can refer to the ORTEP drawing and the data listed in the Supporting Information.

**Acknowledgment.** We thank the National Science Council of the Republic of China for financial support (NCS-88-2113-M-002-019 and -020). We are indebted to Prof. Irina P. Beletskaya for her invaluable discussions.

**Supporting Information Available:** $^1$H and $^{13}$C NMR spectra for compounds **2**, **5**, **8**, **10**, and **12**−**14**, $^1$H,$^1$H 2D-COSY and $^1$H,$^1$H 2D-NOESY spectra for **13** and **14**, and the ORTEP for compounds **2** and **14** are available. This material is available free of charge via the Internet at http://pubs.acs.org.

JO991100U