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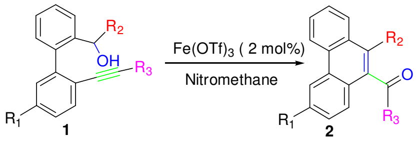

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Iron-catalyzed tandem carbon-carbon/carbon-oxygen bond formation/aromatization of 2′-alkynyl-biphenyl-2-carbinols: A new approach to the synthesis of substituted phenanthrenes

Krishnendu Bera[a] , Soumen Sarkar and Umasish Jana[a,] *

[a] *Department of Chemistry, Jadavpur University, Kolkata 700 032, West Bengal, India*
Fax: +91-33-2414-6584

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ABSTRACT

An iron-catalyzed efficient synthesis of substituted phenanthrenes through tandem intramolecular C-C/C-O bond formations/aromatization of 2′-alkynyl-biphenyl-2-carbinols is reported. This method provides a novel, highly efficient, and straightforward route to 9,10-substituted phenanthrene in good to excellent yields. The present strategy involves tandem $Fe(OTf)_3$-catalyzed generation of benzylic carbocation, 6-*exo-dig* cyclisation of alkyne, carbon-oxygen bond formation and aromatization steps in one pot.

Phenanthrene is of great interest to organic chemist because of their presence in many natural products,[1] and display diverse biological activities such as anticancer,[2] anti-HIV,[3] and antimicrobial activity.[4] Moreover, phenanthrene derivatives also have a wide range of applications in materials science owing to their interesting photo physical properties.[5] In addition, they are also useful intermediates for the synthesis of phenanthrene based alkaloids.[6] Therefore, there is a continued interest in the development new method to construct substituted phenanthrenes.[7] Despite these advances development of a new and efficient method with high atom economy would be highly desirable for the synthesis of diversely substituted phenanthrenes.

Alkynes are reactive structural motifs and have been widely used for a number of atom economical transformations in organic synthesis.[8] During the last few years, several methods have been developed to the synthesis of phenanthrene nucleus via inter- and intramolecular carbocyclisation of alkynes. Among them, metal mediated intramolecular electrophilic annulation of 2-(1-alkynyl)biphenyl derivative have been the most studied method using Ru-, Pt-, ICl/NBS, Fe(III) and combination of disulfide in the presence of Pd/I_2.[9] In addition, Cu(II)-catalyzed coupling/cyclization of terminal alkynes with *N*-tosylhydrazones derived from *o*-formyl biphenyls,[10a] Zn/Cu/TFA-catalyzed domino three-component coupling of biphenyl-2-carbaldehydes/alkynes/piperidine,[10b] Pd-catalyzed annulation of 2,2′-diiodobiphenyls with alkyne,[10c] Cr-mediated coupling of 2,2′-dihalobiphenyl and alkynes in the presence of butyllithium[10d] have also been repoted. Very recently, Au- and In-catalyzed 6-*exo-dig* cycloisomerization of *o*-propargylbiaryls have been demonstrated to afford phenathrene.[11] Therefore, the development of new strategy for the synthesis of phenanthrene is highly desirable in modern organic chemistry.

Iron-catalyzed reactions have recently been emerged as the promising alternatives to traditional transition-metal catalysts because iron is one of the most inexpensive and environmentally friendly metals. As part of our ongoing research program for the development of iron-catalyzed atom-economical reactions for the synthesis of useful organic molecules,[12] very recently, we have reported iron-catalyzed synthesis of phenanthrene via alkyne-carbonyl metathesis.[12f] During our continuous study of iron-catalyzed carbon-carbon bond formation reactions, herein, we report an $Fe(OTf)_3$-catalyzed new synthesis of 9,10-substituted phenanthrene derivatives from 2′-alkynyl-biphenyl-2-carbinols in high yields under extremely mild conditions.

We presumed that 2′-alkynyl-biphenyl-2-carbinols **1** would generate a benzylic carbocation **IA**, and then it might be possible to undergo a carbocation induced ring closure of alkyne via 6-*exo-dig* cyclization that would provide an exocyclic vinylic cation intermediate **1B** which on reacting with in situ generated hydroxide ion or water to produce corresponding dihydrophenathrene derivative **1C**. Serendipitously, we observed that the formation of 9,10-disubstituted phenanthrene **2** occur via insitu oxidation of **1C** (Scheme 1).

To optimize the reaction conditions, at first we investigated the intramolecular tandem reaction of 2′-alkynyl-biphenyl-2-carbinols (**1a**) in the presence of 2 mol% of $FeCl_3$. Pleasantly,

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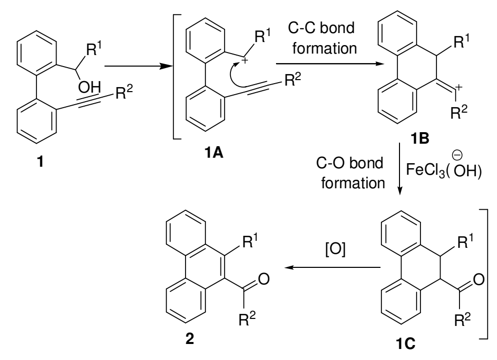
* Corresponding author. Tel.: +03324146666-2535(extention); fax: +-91-33-2414-6584; e-mail: jumasish2004@yahoo.co.in

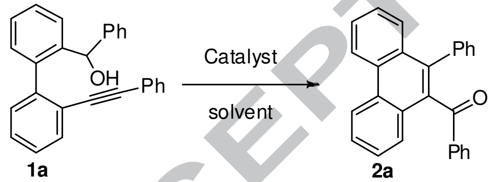
50% of **2a** was obtained in acetonitrile at 60 ^{o}C in 3 h (Table 1, entry 1).

Scheme 1. Strategy for the tandem synthesis of phenanthrenes.



Moreover, it was found that non polar solvent such as toluene did not give any desired product (Table 1, entry 2), whereas 1,2-dichloroethane and nitromethane gave 70% and 75% yields, respectively under heating at 60 ^{o}C. Gratifyingly, a significant improvement was noticed when Fe(OTf)$_3$ (2 mol%) in nitromethane and the yield increased up to 95% (Table 1, entry 5). Then reactivity of various other Lewis acids such as FeBr$_3$, Fe(acac)$_3$, In(OTf)$_3$, AgOTf, AlCl$_3$ and Brønsted acid such as TfOH was studied for this particular transformation, and it was observed that Fe(OTf)$_3$ gave the best result. For instances, FeBr$_3$ gave 85% and Fe(acac)$_3$ produced 50% yield of desired product **2a** (Table 1, entries 6 and 7). On the other hand, In(OTf)$_3$ and AgOTf gave very good yield (90%) under heating at 60 ^{o}C (Table 1, entries 8 and 9) and TfOH gave 80% yield (Table 1, entriy 11), while very strong hard Lewis acid such as, AlCl$_3$ gave only 30% yield (Table 1, entry 10). It is noteworthy that the reaction did not proceed without any catalyst and increasing the amount of catalyst to 5 mol% did not improve the results. So, we decided to use Fe(OTf)$_3$ (2 mol%) in nitromethane to synthesis varieties of 9,10-substituted phenanthrene.

Table 1. Optimization of reaction conditions.^{a}



Entry	solvent	Catalyst (mol %)	Time (h)	Temperature	Yield (%)
1	CH$_3$CN	FeCl$_3$ (2)	3	60 ^{o}C	50
2	Toluene	FeCl$_3$ (2)	1	60 ^{o}C	0
3	1,2-dichloroethane	FeCl$_3$ (2)	1	60 ^{o}C	70
4	Nitromethane	FeCl$_3$ (2)	1	60 ^{o}C	75
5	**Nitromethane**	**Fe(OTf)$_3$ (2)**	**2**	**r.t.**	**95**
6	Nitromethane	FeBr$_3$ (2)	1.5	r.t.	90
7	Nitromethane	Fe(acac)$_3$ (2)	8	r.t.	50
8	Nitromethane	In(OTf)$_3$ (2)	2	60 ^{o}C	90
9	Nitromethane	AgOTf (2)	2	60 ^{o}C	90
10	Nitromethane	AlCl$_3$ (2)	10	r.t.	30
11	Nitromethane	TfOH (2)	5	r.t.	80

^{a}Reaction Conditions: **1a** (0.5 mmol), catalyst (0.01 mmol) and solvent (3 mL).

The compound 2a was characterized by NMR, HRMS and X-ray crystallography structure (Fig 1, CCDC no. 1024586).

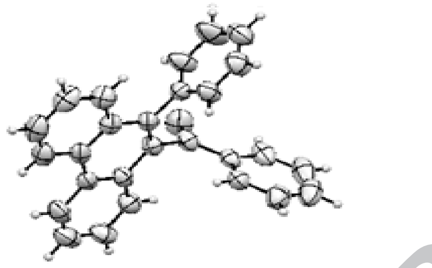
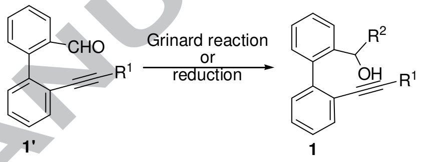


Fig. 1 ORTEP diagram of **2a.**

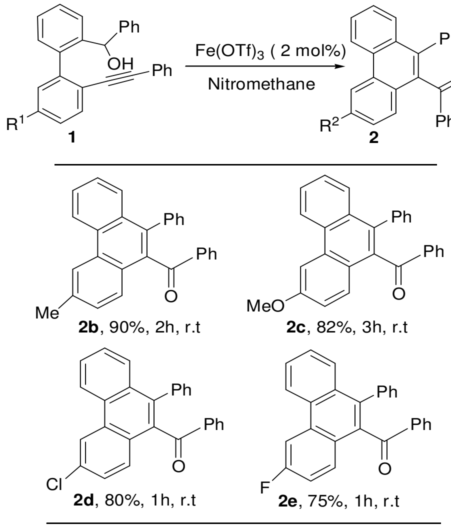
To better understand the potentiality of the new synthesis, various 2´-alkynyl-biphenyl-2-carbinols were prepared from corresponding 2´-alkynyl-biphenyl-2-carbaldehydes by reacting with Grignard reagents or reduction (Scheme 2). Substituted 2´-alkynyl-biphenyl-2-carbaldehydes could easily be prepared according to our previous method.[12]

Scheme 2. Preparation of 2´-alkynyl-biphenyl-2-carbinols.



First, the influence of the substitution on the aromatic ring of biphenyl ring connected to the alkyne unit was studied (Scheme 3, entries **2b-2e**). The yields were good to excellent regardless of substitution patterns on the aromatic ring of the biphenyl system bearing alkyne. For instances, all the *p*-Me (**2b**), *p*-OMe (**2c**), *p*-Cl (**2d**) and *p*-F (**2e**) substituted phenanthrene derivatives were obtained 90%, 82%, 88% and 85% yields, respectively. The results indicated that nature of the substituents on the aromatic ring of biphenyl ring connected to the alkyne did not have any strong electronic influences.

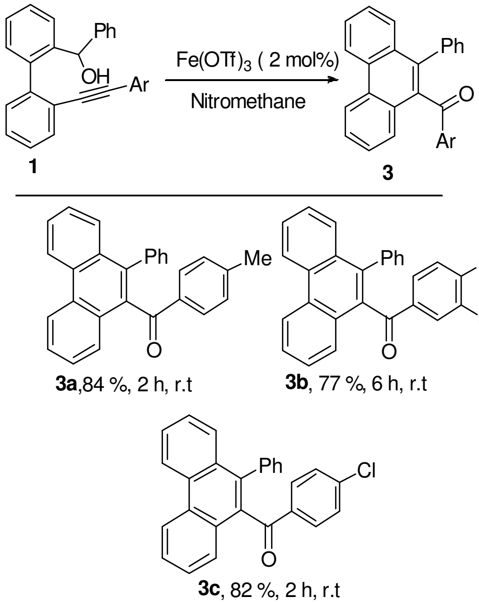
Scheme 3. Fe(OTf)$_3$ catalysed synthesis of substituted phenanthrenes.^{a}



^{a}Reaction Conditions: Substrate **1** (0.5 mmol), Fe(OTf)$_3$ (0.01 mmol) and nitromethane (3 mL).

Next, we investigated the effect of substitution on the aromatic ring of alkyne unit (Scheme 4). Pleasantly, we observed that both electron-donating groups such as methyl and methoxy groups, and weakly electron-withdrawing group such as chloride were suitable on the aromatic ring of alkyne moieties and afforded the corresponding substituted phenanthrenes in good yields 84%, 77% and 82%, respectively at room temperature within a short period of time (Scheme 4, entries **3a**-**3c**). Unfortunately, alkyl substituted alkyne gave mixture of products.

Scheme 4. $Fe(OTf)_3$ catalysed synthesis of substituted phenanthrenes.[a]



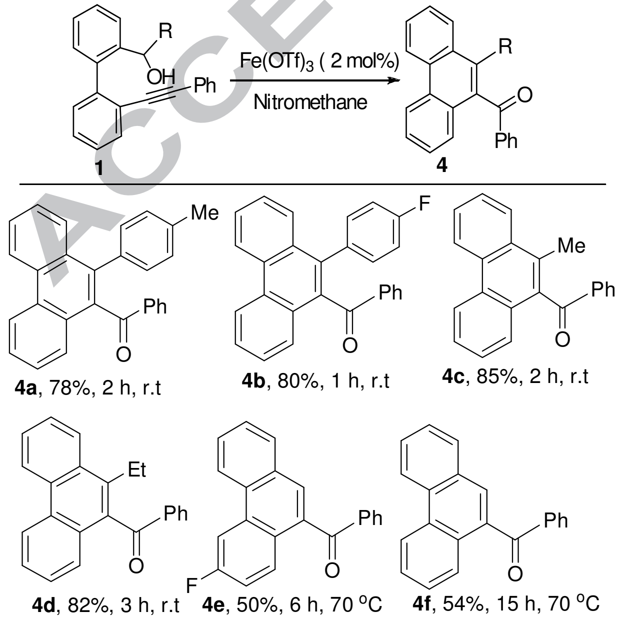
3a,84 %, 2 h, r.t **3b**, 77 %, 6 h, r.t

3c, 82 %, 2 h, r.t

[a] Reaction Conditions: Substrate (0.5 mmol), $Fe(OTf)_3$ (0.01 mmol) and nitromethane (3 mL).

Finally, the scope of this $Fe(OTf)_3$-catalyzed tandem intramolecular carbon-carbon/carbon-oxygen bond formation and subsequent aromatization was also studied with varieties of substitution at alcoholic centre. The result has been summarized in scheme 5. It was observed that substitution on aromatic ring at alcoholic center such as *p*-Me and *p*-F were also well tolerated and undergo smooth cyclisation leading to the desired products in high yields 78% and 80%, respectively (Scheme 5, entries **4a** and **4b**). In addition, benzylic alcohols bearing alkyl groups (such as methyl and ethyl) also reacted smoothly and furnished desired substituted phenanthrenes **4c** and **4d** in excellent yields (Scheme 5, 80% and 82%) without any elimination product. Moreover, we found that less reactive primary benzylic alcohol containing substrates were also reacted in the presence of 2 mol% $Fe(OTf)_3$ and gave the desired 9-benzoyl phenanthrenes **4e** and **4f** in 50 % and 54%, respectively. However, due to less stability of primary benzylic cation, it required higher temperature (70 °C) and gave lower yields of the desired products.

Scheme 5. $Fe(OTf)_3$ catalyzed synthesis of substituted phenanthrenes.[a]



4a, 78%, 2 h, r.t **4b**, 80%, 1 h, r.t **4c**, 85%, 2 h, r.t

4d, 82%, 3 h, r.t **4e**, 50%, 6 h, 70 °C **4f**, 54%, 15 h, 70 °C

[a] Reaction Conditions: Substrate **1** (0.5 mmol), $Fe(OTf)_3$ (0.01 mmol) and nitromethane (3 mL).

In general all the reactions proceeds smoothly via a cationic cyclisation with alkyne in 6-*exo-dig* manner.[13] Although the addition of a carbocation to unsaturated carbon-carbon functionalities represents a well-established strategy for the carbon-carbon bond formation in the synthesis of complex organic molecules.[14] To the best of our knowledge this is the first synthesis of phenanthrene via intramolecular addition of alkyne with benzylic cation in the presence of iron-salt. The mechanism of this reaction has been delineated in Scheme 1. Although, the generation of benzylic carbocation **1A**, cyclistion to **1B** and formation of **1C** are very logical and starightforward; however, the mechanism of facile oxidation to phenanthrene derivative is not very clear. Presumably, aerial oxidation is the main path way for this step as the reaction was carried out in the presence of air. However, when the reaction was carried out under argon atmosphere the mixture of compounds were formed including the desired product in lower yield. Moreover, nitromethane may also take part in this oxidation process as better yield was obtained in nitromethane.

In conclusion, we have developed a new and efficient method for the synthesis of various functionalized phenanthrenes in good to excellent yields from readily available 2′-alkynyl-biphenyl-2-carbinols derivatives. Importantly, this method would be a versatile alternative of existing methods to install the substitution at 9,10-position of phenanthrenes. Moreover, the reaction is highly atom efficient and environmentally benign as inexpensive and non toxic iron is used catalyst and no byproduct is formed. The reaction works under extremely mild conditions with low catalyst loading (2 mol%).[15] Considering all these advantages, we believe that the present synthetic strategy may find application to synthesis phenanthrene based biologically active molecules. Further related investigations are underway.

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15. Representative experimental procedure for the preparation of phenanthrene (**2a):**
    Compound **1a** (179 mg, 0.5 mmol) was taken in a 10 mL round bottom flask containing 3 mL of dry nitromethane and fitted with CaCl$_2$ gurd tube. Anhydrous Fe(OTf)$_3$ (5.50 mg, 0.01 mmol) was added to it and the reaction mixture was stirred for 2h at room temperature. After completion of the reaction (TLC), nitromethane was distilled out under reduced pressure and the residue was purified by silica gel (mesh 100-200) column chromatography (petroleum ether/EtOAc) to afford **2a** (170 mg, 0.48 mmol, 95 %) as a white solid. m.p. 144 ^{0}C. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.10 (brs, 2H), 7.22–7.26 (m, 3H), 7.40–7.45 (m, 3H), 7.51–7.56 (m, 2H), 7.64 (d, J = 7.8 Hz, 3H), 7.70 (t, J = 7.8 Hz, 3H), 8.02 (d, J = 8.4 Hz, 2H) ppm.^{13}C NMR(CDCl$_3$, 75 MHz) δ 122.7, 122.9, 126.5, 127.0, 127.1, 127.3, 127.6, 128.3, 129.0, 129.5, 129.9, 130.7, 131.1, 133.2, 135.7, 135.8, 137.2, 138.2, 199.4 ppm. HRMS: calcd. for C$_{27}$H$_{19}$O [M+H] 358.1358; found 358.1354.