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# 1,4-Diaryl-1,3-butadiyne: A powerful synthon for the $PhI(OAc)_2$ mediated synthesis of Highly substituted naphthalene via carbocyclization

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**Abstract:**

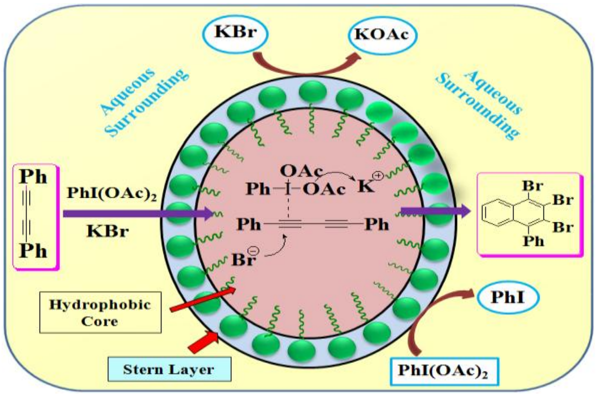
A $PhI(OAc)_2$/KBr mediated facile, efficient and highly convergent route has been achieved for the synthesis of 1,2,3-tribromo 4-aryl naphthalenes from 1,4-diaryl-1,3-butadiynes via electrophilic carbocyclization in water medium. Aqueous KBr acts as the bromide source in presence of hypervalent iodine $PhI(OAc)_2$, which promotes the carbocyclization reaction. This rapid and safe process established itself as a very interesting synthetic route for the synthesis of 1,2,3,4-tetra substituted naphthalene moiety. 1,3-Diynes are insoluble in water; and to overcome this issue, the reaction was planned within micelles using of CTAB surfactant.

**Keywords:** 1,3-Diynes, CTAB, $PhI(OAc)_2$, Green bromination, Tetra substituted naphthalene

## Introduction:

Fundamental organic reactions are now frequently studied in surfactant-assembled aqueous micelles of nanoscale dimension.[1] To avoid the insolubility problem of organic precursors and reagents in water medium, organic reactions are now studied in presence of surfactant in aqueous medium towards the green and sustainable development in chemistry.[2]

Poly-substituted naphthalenes are important motif in view of chemical and pharmaceutical industries so their new synthetic methodologies are always an important area towards organic chemists.[3] Their rigid molecular structure have played an important role to advance in a number of areas of chemical research such as host-guest chemistry,[4] liquid crystal chemistry,[5] and even biochemical studies of synthetic peptides.[6] They are also important, in a number of advanced technologies utilizing nonlinear optical (NLO),[7] photo, and electroluminescent,[8] and molecule-based sensory devices.[9] Therefore, in spite of recent advances, the development of a more flexible and efficient methodology for the synthesis of poly substituted naphthalene is still important towards organic chemists. Recently Miura and co-workers have reported the synthesis of highly substituted naphthalenes via rhodium catalyzed oxidative coupling of aryl boron compounds with alkynes in intermolecular fashion.[10] From careful literature survey it was seen that only one synthetic method available for synthesis of 1,2,3-tribromo 4-aryl naphthalenes from 1,4-diaryl-1,3-butadiynes which was reported by Singha et al. by using molecular bromine at -78 $^{0}$C.[11] But the use of molecular bromine is very much risky and bromine vapour is highly toxic for human health.

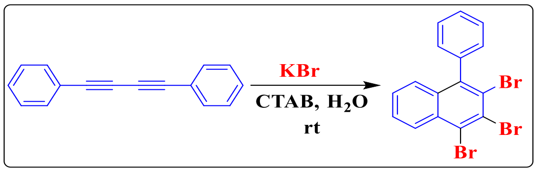


**Scheme-1**. Synthesis of 1,2,3-tribromo naphthalene within micelles

Greener approaches and sustainable processes are the prime interest towards the organic chemists. Herein a facile synthesis of 1,2,3,4-tetra substituted naphthalenes has been achieved into nanoscale aqueous micelles by using PhI(OAc)$_2$ and KBr for the bromine source (Scheme 1).[1] From the careful literature survey, it was seen that 1,4-diaryl-1,3-butadiyne has been extensively used for various heterocycles and carbocycle.[12] It is a very important starting material as well as substrate used in organic synthesis and for fabricating various important materials. Various 1,4-Diaryl-1,3-buta diynes have been prepared from the terminal alkynes (phenyl acetylene and its derivatives) using 5 mol% of CuCl and 1.0 mmol of piperidine in DCM at room temperature stirring for 30-45 min.

Being most abundant and environmentally safe, water is the solvent of our choice for development of a cleaner and more benign carbocylization reaction using KBr as the direct source of bromine. In 2011 Maiti et al reported a process of activation of π-bonds (alkenes, alkynes) with cationic surfactant and direct transfer of halides from alkyl halides (NaX, X = Cl, Br, I) to alkyne and alkene to afford α, α-dihaloketones and other valuable synthons with outstanding selectivity.[2d] Then, we have envisioned upon activation of π-bond of 1,4-diphenyl-1,3-butadiyne with a hypervalent iodine inside a surfactant-assembled lipophilic nanoreactor which shows that it can accept $Br^-$ from an aqueous surrounding (Scheme 1). And upon treatment of our model substrate 1,4-diphenyl-1,3-butadiyne (**1a**, entry 2, Table 1) with π-bond activator PhI(OAc)$_2$, cationic surfactant CTAB and KBr at room temperature in aqueous medium shows that, $Br^-$ is transferred very rapidly (15 min) to afford 1,2,3-tribromo naphthalene **2a**. To optimize the reaction condition, we have performed same set of reactions under various conditions and the results in details have been summarized in **Table 1**. Anionic (SDS) and neutral Tween 80 could not transfer Br (entries 3, 4). We have examined two polymeric hypervalent iodanes (entry 4 & 5) but they are not fruitful towards this transformation and reaction profiles were not clear. Simple molecular iodine was tested and was found as inactive for this transformation (Entry 6). Next, we have checked the role of KI and KCl for this carbocyclization reaction but several spots were found in the TLC. So from these observations it was clear that PhI(OAc)$_2$/KBr in presence of CTAB is the best condition for this transformation.

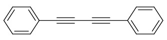
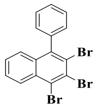
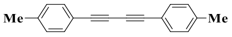
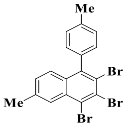
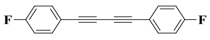
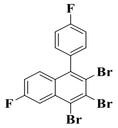
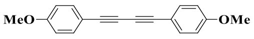
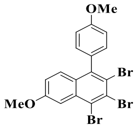
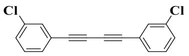
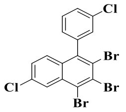
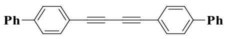
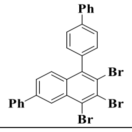
**Table 1.** Optimization of reaction condition



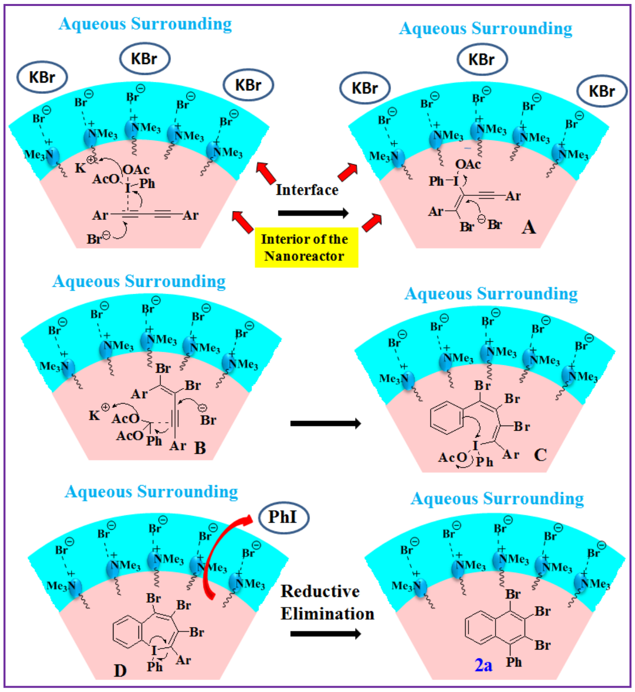
| Entry | Reagent (mmol) | Solvent/ Surfactant | Reaction Time (min) | Yield (%) |
|---|---|---|---|---|
| 1 | KBr | $H_2O$/CTAB | 30 | - |
| 2 | $PhI(OAc)_2$ /KBr (3:3) | $H_2O$/CTAB | 15 | 80 |
| 3 | $PhI(OAc)_2$ /KBr (1:1) | $H_2O$/SDS | 15 | - |
| 4 | $PhI(OAc)_2$ /KBr (1:1) | $H_2O$/Tween 80 | 15 | - |
| 5 | PhIO/KBr (3:3) | $H_2O$/CTAB | 30 | Trace |
| 6 | PhINTs/KBr (1:1) | $H_2O$/CTAB | 30 | Trace |
| 7 | $I_2$ | $H_2O$/CTAB | 30 | 0 |
| 8 | KI | $H_2O$/CTAB | 30 | - |
| 9 | KCl | $H_2O$/CTAB | 30 | - |

To justify and elaborate the scope of the methodology we have prepared various 1,4-diaryl-1,3-butadiens under the above optimize reaction condition and all responded to this methodology in very good yield (**Table 2**).

**Table 2.** Synthesis of 1,2,3-tribromo-4-aryl naphthalene

| Entry | Reactant | Reaction time (min) | Product | Yield (%) |
|---|---|---|---|---|
| 1 |  | 10 |  | 85 |
| 2 |  | 10 |  | 87 |
| 3 |  | 12 |  | 88 |
| 4 |  | 15 |  | 77 |
| 5 |  | 20 |  | 80 |
| 6 |  | 30 |  | 72 |

On the basis of the experimental results obtained we have proposed a plausible reaction mechanism of this carbocyclization reaction which has been depicted in Scheme 3. In the first step, $PhI(OAc)_2$ activates the triple bond and the $Br^-$ inserted into the alkyne to give the intermediate **A**. Then, another $Br^-$ inserted similarly to give the intermediate **B**. Another molecule of $PhI(OAc)_2$ activates the other triple bond and then attack of $Br^-$ occurs to give **C**. The next step is the elctrophilic cyclization to give the intermediate **D,** which upon reductive elimination followed by ring contraction gives the product **2**.



**Scheme3.** Plausible reaction mechanism of 1,2,3-tribromo-4-phenyl napthalene

**Reaction Procedure:** In a 25 mL round bottom flask 5 mL of water was taken in presence of 50 mg of CTAB and 1 mmol of 1,4-diaryl-1,3-butadiyne and it was stirred very well for 1 minute. Then 2 mmol each of $PhI(OAc)_2$ and KBr were added to it. Progress of the reaction was monitored by TLC and after the completion of the reaction, the sticky solid was separated out from the water medium. To this reaction mixture 20 mL of DCM was added and extracted twice. Combined organic layer was dried over $Na_2SO_4$ and evaporated under vacuum. Crude reaction mixture was purified by column chromatography using 100:200 mesh silica gel and *n*-hexane as eluent to obtain the pure product.

## Conclusions:

In conclusion, we have developed a $PhI(OAc)_2$ / KBr mediated facile green approach for the rapid access of 1,2,3-tribromo naphthalenes in water medium in short reaction time to get very good yield. The reaction occurs in the surfactant- assembled aqueous micelles of the nanoscale dimension. PhI is the only bi-product formed in the reaction process. The ease of handling, and easy purification of the product makes the process very much attractive.

## Acknowledgement

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