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PII: S0040-4039(16)31007-3
DOI: http://dx.doi.org/10.1016/j.tetlet.2016.08.020
Reference: TETL 47991

To appear in: *Tetrahedron Letters*

Received Date: 12 June 2016
Revised Date: 5 August 2016
Accepted Date: 6 August 2016

Please cite this article as: Dixit, S., Siddiqui, Q.T., Muneer, M., Agarwal, N., Ferrocene catalysed C-H arylation of arenes and reaction mechanism study using cyclic voltammetry, *Tetrahedron Letters* (2016), doi: http://dx.doi.org/10.1016/j.tetlet.2016.08.020

Graphical Abstract

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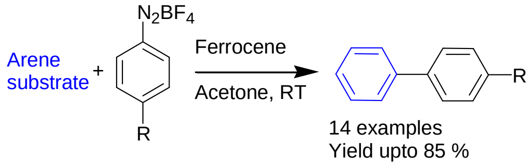

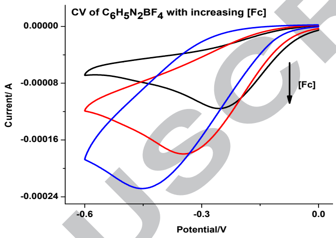

Cyclic voltammetry provides insight on the radical formation in the initial steps of reaction

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ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

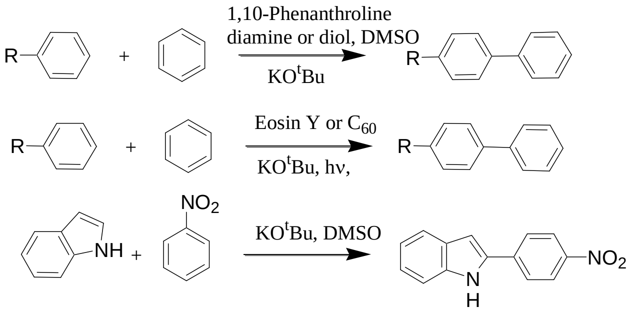
Keywords:
C-H arylation
Ferrocene
Catalysis

ABSTRACT

Ferrocene catalysed C-H arylation of benzene using aryldiazonium salt is studied. Yield of biphenyl in this reaction was found to be better than some of the known methods. Aryldiazonium salts with electron withdrawing groups produced excellent yields (upto 85%) in C-H arylation. Applicability of this reaction was studied on several arenes and heteroarene such as benzene, naphthalene, anthracene, pyrene and pyridine. Catalytic role of ferrocene in aryl radical formation was studied by cyclic voltammetry of phenyldiazonium tetrafluoroborate. In presence of ferrocene more radical formation was observed. This reaction model works at ambient temperature and features the use of inexpensive catalyst for the synthesis of biaryl derivatives.

Biaryl motifs have several applications in areas such as synthesis of catalysts, synthesis of chiral ligand, optoelectronic materials, enzyme inhibitors and medicines.[1] Several cyano biphenyls with long aliphatic tails are in demand for commercial grade liquid crystal display technologies and in organic light emitting devices.[2] A class of dye family derived from benzidine is popularly used in commercial dyes and polymers.[3] Biaryls with different substituents are commonly used as building blocks for synthesis of polycyclic aromatic compounds.[4] Synthesis of biphenyls or biaryls require the carbon-carbon bond formation (C-H arylation) and can be achieved by several methods. Some of the classical methods are Ullmann reaction, Scholl reaction, Gomberg-Bachmann reaction, Grignard reaction etc.[5] The yield in these reactions is poor, also they have very limited applications due to sensitive reaction conditions. Several groups have reported the synthesis of biaryls using transition metal catalysed coupling reactions (e.g. Suzuki, Negishi, Stille, Kumada, Hiyama etc).[6] These coupling reactions require aryl halides/triflates and coupling partners such as boronic acids, sodium sulfinates, silanes, and organotin compounds. Later, copper and silver catalysed coupling between aryl boronic acids and heteroaryls were developed.[7,8] Unarguably transition metal catalyzed approaches are very popular to synthesize biphenyl derivatives.[9] However, these methods are not suitable for the synthesis of biaryls for biological applications due to inherent toxicity of some transition metals. Also, these methods are not economically viable.

In recent times, addition of aryl radicals to arenes followed by elimination of hydrogen radical have been reported. Several methods have been developed for the aryl radical formation reactions. Dediazoniation of aromatic diazonium salts, aryl halides with radical generator have been used as aryl radical source albeit with limited use. Transition metal-free approaches have emerged as an alternate choice for aryl-aryl couplings (Scheme 1).



Scheme 1: Transition metal-free approaches for C-H arylation

In 2009, Itami et al reported KO^{t}Bu promoted coupling of heteroarenes with aryl iodides.[10] Shi et al,[11] Hayashi et al[12] and other groups[13] reported the similar synthesis of biaryls using

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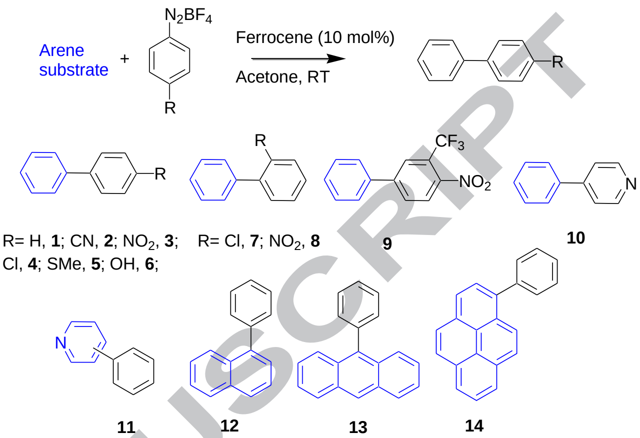
unactivated arenes and aryl halides in the presence of base. In some of these cases N-heteroaryl ligands, or catalytic amount of diamine and diols were also used as ligand. Ligand binds with metal ion to form an intermediate and promotes the single electron transfer.[14] Rossi et al and Li et al recently showed light driven (photocatalytic) direct arylation of benzene with KO^{t}Bu in DMSO.[15] Konig et al developed metal and base free Eosin Y catalysed photocatalytic approach for CH arylation.[16] Chan et al used porphyrin, phthalocyanine and fullerene as organocatalyst for C-H arylation.[16b-e] Very recently Sangit et al explored the use of KO^{t}Bu-mediated C-C coupling in phenols and benzamides using aryl halide coupling partners.[17a,b] Same group has reported the KO^{t}Bu-mediated intermolecular oxidative C-C coupling of nitroarenes with indoles.[17b]

The arylation of benzene and other accessible bromoarenes require the use of light, heat and catalyst to get the aryl-aryl bond formation. Yuan et al recently showed the direct arylation of benzene with aryl halide and 1,10-phenanthroline and KO^{t}Bu.[18] These reaction conditions ensure the aryl radical formation as the intermediate which was proved by electron papamagnetic resonance (EPR) methods. Ferrocene catalysed efficient and cost effective reaction for C-H arylation of BODIPY using phenyldiazonium tetrafluoroborate was developed.[19] Ferrocene in this reaction is believed to catalyze the aryl radical formation which prompted us to use aryldiazonium salt for the direct arylation of benzene. Here, in this report, we studied the general applicability of ferrocene catalysed arylation on several arenes and heteroarene such as benzene, naphthalene, anthracene, pyrene and pyridine. Catalytic role of ferrocene in the formation of aryl radical was studied by cyclic voltammetry of aryldiazonium tetrafluoroborate in the presence of ferrocene. This reaction model works at ambient temperature and features the use of inexpensive catalyst for the synthesis of biaryl derivatives.

Aryldiazonium tetrafluoroborates were prepared using aryl amines and tetrafluoroboric acid (HBF_4). Aryl amine was dissolved in aqueous solution of HBF_4 at 0 °C and solution of $NaNO_2$ at 0 °C was added to it slowly. Aryldiazonium tetrafluoroborate precipitated out during the reaction. On completion of reaction solid was filtered and washed with cold water. Various aryldiazonium tetrafluoroborate salts bearing electron-withdrawing or electron-donating groups were synthesized. These freshly prepared aryldiazonium tetrafluoroborates were used to synthesize the biaryl derivatives. To optimize the reaction conditions, phenyldiazonium tetrafluoroborate and benzene were used as reactants and acetone as solvent. Ferrocene dissolved in acetone was used as catalyst. Reaction of phenyldiazonium tetrafluoroborate (1 eq), benzene (3 eq) and ferrocene (10 mol%) in acetone proceeded smoothly at room temperature in 2 h. The desired 1,1'-biphenyl was obtained in 84% yield. The yield obtained in this reaction is found to be higher than some of the literature methods. A few other organic solvents such as dichloromethane, DMSO and DMF were also tested as reaction medium to understand the suitability and adaptability of this reaction. Poor yields (less than 30%) were obtained in DMSO and acetonitrile while no reaction was observed in dichloromethane probably due to insolubility of aryldiazonium salt. Solvents such as $CHCl_3$ and THF produced a complex mixture of products. In the absence of ferrocene reaction proceeds very slowly and produced biphenyl in poor yield (~ 10%).

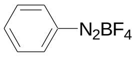
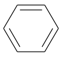
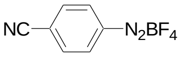
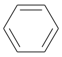
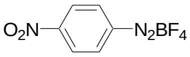
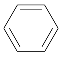
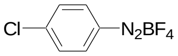
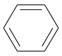
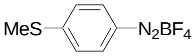
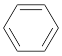
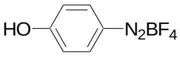
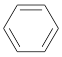
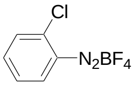
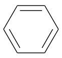
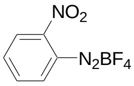
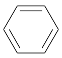
Several derivatives of aryl and heteroaryl diazonium tetrafluoroborate were used to synthesize the biaryl derivatives (Table 1). The yield of the products depends, fairly, on the inductive effect of groups present on aryldiazonium salts. It was found that excellent yields were obtained when electron-withdrawing groups were substituted on phenyl (**2-4** of Table 1). Electron-donating groups produced lesser yield of biaryls (**5, 6** of Table 1). Groups *ortho* to amino also produced relatively lesser yield (**7, 8** of Table 1) and can be attributed to steric effect.

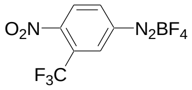
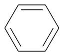
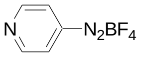
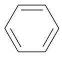
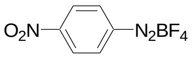
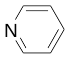
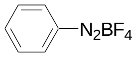
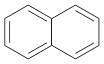
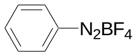
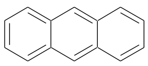
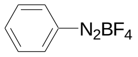
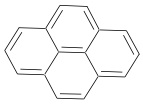


Scheme 2: Synthesis of ferrocene catalysed biaryl derivatives.

This method of arylation is applicable to various arene substrates such as naphthalene, anthracene and pyrene and also on heteroarene such as pyridine. In general, yields obtained are good to excellent. In some examples, yield obtained is better than the previously reported methods. All these compounds were characterized by several spectroscopic methods. Experimental details and related spectra are provided in supporting information.

Table 1: Arylation of arenes with aryldiazonium tetrafluoroborate

Aryl diazonium salt	**Arene**	**^{a}Yield (%)**	**Product**
		84	**1**
		85	**2**
		81	**3**
		75	**4**
		57	**5**
		44	**6**
		67	**7**
		78	**8**

Aryl diazonium salt	Arene	^{a}Yield (%)	Product
		82	**9**
		67	**10**
		81	**11**
		56	**12**
		42	**13**
		21	**14**

^{a}Isolated yields

Dehaen et al. have proposed a radical reaction mechanism for ferrocene catalysed C-H arylation on BODIPY. We recently studied similar reaction using EPR experiments and found evidences of radical formation in initial steps which was further supported by DFT calculations.[19b] Aryl diazonium salts usually accept single electron to form aryl radicals.[20] Aryl radicals formed may undergo several possible reactions (i) homo-coupling of radical, (ii) abstraction of protons from solvents in turn production of solvent radicals, and so on.[21] To get the insight on the reduction and, eventually, the radical formation of phenyldiazonium tetrafluoroborate we studied the electrochemical behavior of phenyldiazonium tetrafluoroborate using cyclic voltammetry. The figure 2 shows the voltammogram of phenyldiazonium tertrafluoroborate in acetonitrile (6.5 mM) on glassy carbon as working electrode at a scan rate of 1 V/sec. A broad irreversible wave ($^{red}E_p$) was observed at -0.25 V/Ag,AgCl. Irreversibility of reduction peak indicates the dissociation of diazonium salt on electron transfer. Tiny bubbles were visible in solution during the potential scan, possibly evolution of nitrogen gas. Further, on second scan this reduction peak shifted towards more negative potential and later in successive scans disappeared. In higher concentration of phenyldiazonium tetrafluoroborate similar shift in the reduction potential was observed however no reduction peak was observed when very high concentration (13 mM) or slow scan rate (50 mV/sec) was used. Pinson et al explained this on the basis of reaction of phenyl radicals with active electrode area which causes the changes in electrode property.[21b]

To study the effect of ferrocene on reduction of aryldiazonium salt we carried out the cyclic voltammetry of a mixture of salt and increasing concentration of ferrocene (0-0.15 µM). Glassy carbon electrode was washed and cleaned thoroughly after every measurement to nullify the effect of electrode blocking. Reduction current was found to be increasing with increase of ferrocene concentration while having the constant concentration of phenyldiazonium tetrafluoroborate. Also peak potential shifted towards more negative values. Increase in current as well as shifting of reduction peak potentials with increasing concentration of ferrocene suggests the formation of more phenyl radicals (Figure 1). These results suggest that ferrocene is catalyzing the formation of phenyl radicals. Aryl radical generation through single electron transfer should be prominent in case of electron deficient aryl diazonium salts and hence results in better yields (**2-4**).

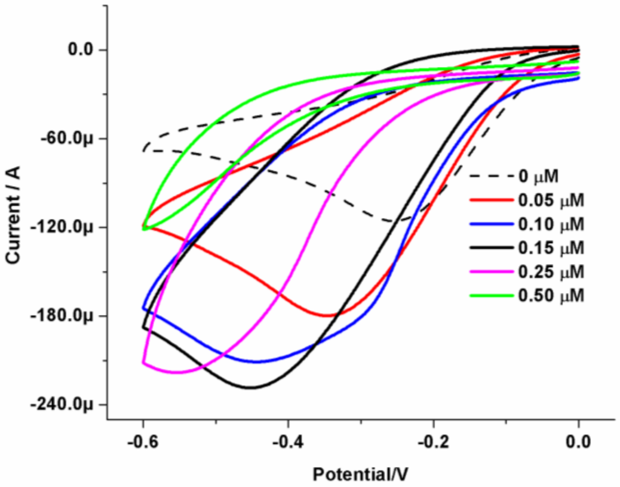


Figure 1. Cyclic voltammograms of phenyldiazonium tetrafluoroborate (6.5 mM) with increasing concentration of ferrocene recorded in acetonitrile.

Reaction mechanism for ferrocene catalysed C-H arylation is expected to be radical mediated as proposed in Figure 2. In the initial step, single electron transfer (SET) from ferrocene to aryldiazonium salt produces aryl radical which further takes part in the reaction. We investigated the formation of aryl radicals by cyclic voltammetry. The formed aryl radical reacts with arene followed by electron transfer to ferrocenium ion and subsequently hydrogen abstraction to complete the reaction. Aryl radical generation from diazonium salts is believed to be a fast reaction and is unlikely to be the rate determining step. To get an insight on the rate determining step competition reaction between benzene and benzene-d$_6$ is carried out. The K_H/K_D value was determined by the ^{1}H NMR (See supporting information) and is found to be ~ 1 which implies that C-H bond cleavage is not rate determining step. On the basis of these results the rate-determining step may be the bond formation between aryl radical and arene.

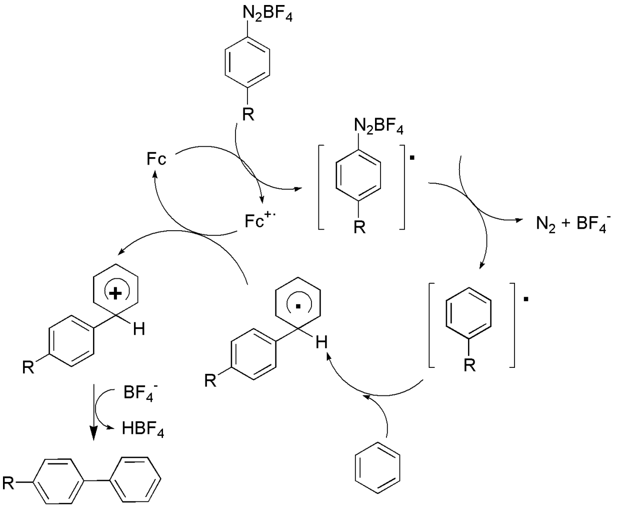


Figure 2: Proposed reaction mechanism for ferrocene catalysed C-H arylation.

Conclusions

Ferrocene catalysed C-H arylation of benzene using phenyldiazonium tetrafluoroborate is studied. Yields of biphenyl derivatives in this reaction were found to be better than some of the known methods. Aryl radical formation is studied by cyclic voltammetry of aryldiazonium tetrafluoroborate. More radical formation was observed in the presence of ferrocene. Applicability of this reaction is tested on several arenes and heteroarene such as benzene, naphthalene, anthracene, pyrene and pyridine. This reaction model works at ambient temperature and features the use of inexpensive ferrocene as catalyst.

Supporting Information:

Synthesis, characterization data, NMR, MALDI and FTIR spectra of selected compounds are given in supporting information.

Acknowledgements

Centre for Excellence in Basic Sciences, Mumbai is thanked for providing research facilities. We also thank Tata Institute of Fundamental Research, Mumbai for providing the NMR and MALDI-TOF facilities.

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Highlights

- Synthesis of biaryl derivatives using ferrocene as catalyst is described
- Arenes and aryldiazonium tetrafluoroborate were used as reactants
- C-H arylation was successfully employed on several arenes
- Reaction pathway was studied using cyclic voltammetry
- Ferrocene catalysed C-H arylation is elegant and simple to perform