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Friedel–Crafts Arylation for the Formation of C_{sp^2}–C_{sp^2} Bonds: A Route to Unsymmetrical and Functionalized Polycyclic Aromatic Hydrocarbons from Aryl Triazenes**

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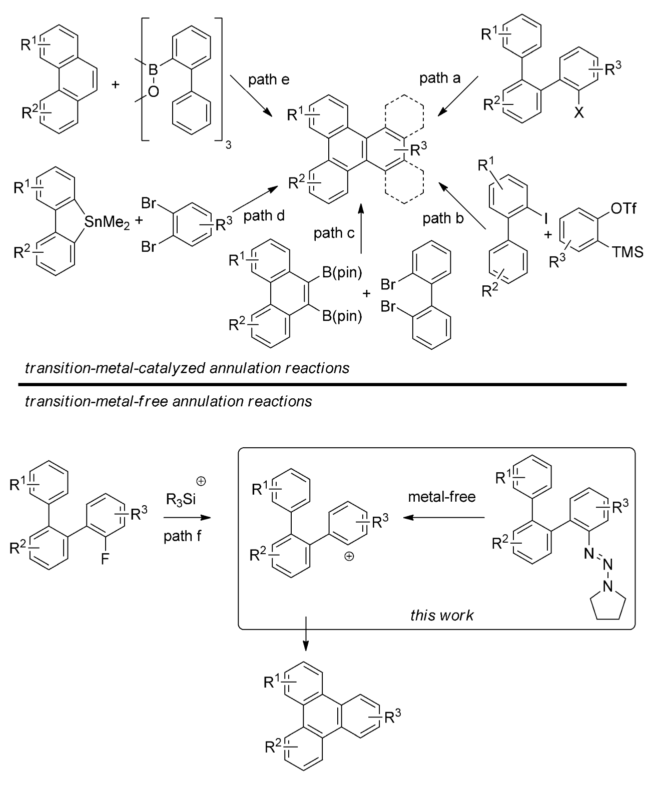
Because of their special optical and electronic properties, the efficient synthesis of unsymmetrical and functionalized polycyclic aromatic hydrocarbons (PAHs) is becoming much more important.[1] The transitionmetalcatalyzed cross-coupling reactions of organometallic reagents with organic halides are popular methods for the formation of C_{sp^2}–C_{sp^2} bonds.[2] Thus, transition-metal-catalyzed annulation reactions of functionalized precursors, such as intramolecular direct arylations (Scheme 1, path a),[3] the annulation of arynes[4] (path b), double-coupling reactions of organodimetallic reagents with dihalides[5] (paths c and d), sequential C–H arylation with *o*-biphenylboroxin and $FeCl_3$ oxidation (path e),[6] and [2+2+2] or [4+2] cycloaddition reactions,[7] provide effective synthetic transformations for the synthesis of functionalized PAHs. Moreover, oxidative dehydrogenation coupling reactions are also a feasible way to construct PAHs, and $FeCl_3$ is a popular oxidant.[8]

Compared to transition-metal-catalyzed crosscoupling reactions, the Friedel-Crafts reaction is a classic carbon-carbon bond ($C_{sp^2}C_{sp^3}$ bond) formation reaction that can be carried out in the presence of a Lewis acid catalyst, such as BF_3, $FeCl_3$, or $AlCl_3$, to couple an aromatic ring with an alkyl halide or acyl halide through a carbocation intermediate.[9] With respect to C_{sp^2}–C_{sp^2} bond formation, the Friedel-Crafts reaction shows limited utility, owing to the instability of the phenyl cation and a bottleneck in generation.[10] Recently, in a new take on the reaction, Allemann and co-workers reported an acid-catalyzed, silane-fueled Friedel–Crafts coupling of fluoroarenes (path f).[11,12] This catalytic process includes C–F bond activation and C–C bond formation.

Arenediazonium salts, an excellent precursor for generation of phenyl cation and radical intermediates, were thoughly investigated by Zollinger et al.[13] and others.[14] As a protected arenediazonium salt equivalent, aryltriazene has been used as a critical synthon for the construction of C–X (X = halides, CN, and N_3) bonds, however, few examples were reported for the construction of C_{sp^2}–C_{sp^2} bonds.[15] In our previous work, triazene unit acts as a leaving group in the presence of $BF_3{\cdot}OEt_2$, so as to synthesize a number of highly substituted carbazoles, dibenzofurans, and dihydrobenzofurans in a regioselective manner.[16] Thus, we had the idea that aryltriazene could potentially act as an aryl cation precursor. If this precursor was attacked by another aryl, a new aromatic ring would form, which would provide an effective synthesis of a series of PAHs.



Scheme 1. Strategies for the synthesis of PAHs. pin = pinacol, Tf = trifluoromethanesulfonyl, TMS = trimethylsilyl.

Herein, we report a Friedel-Crafts intramolecular arylation for the synthesis of polycyclic aromatic hydrocarbons from aryl triazenes. This approach involves treating readily available aryl triazenes (Scheme 1) with $BF_3{\cdot}OEt_2$, which serves as a Lewis acid to promote the formation of a phenyl cation. This highly activated phenyl cation intermediate is then be attacked by a *meta*-substituted aryl group, followed by intramolecular arylation. This method can be used to

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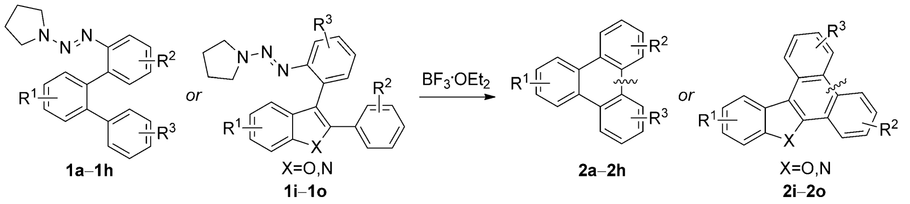
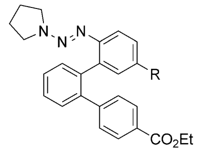
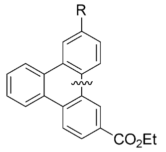
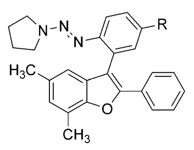
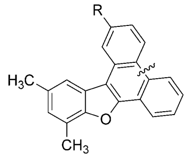
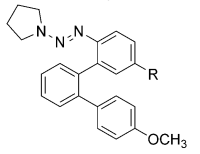
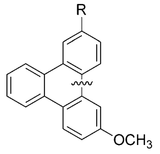
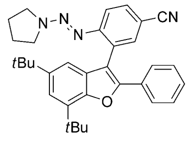
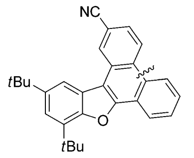
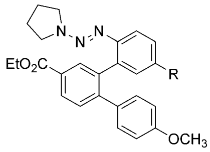
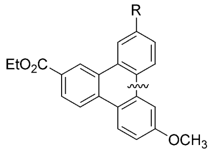
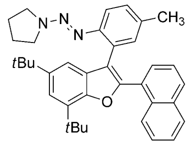
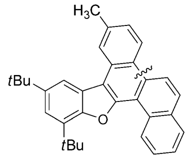
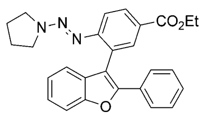
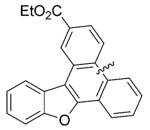
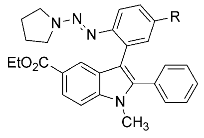
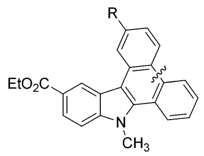
Table 1: Synthesis of six-membered rings from aryltriazenes.[a]



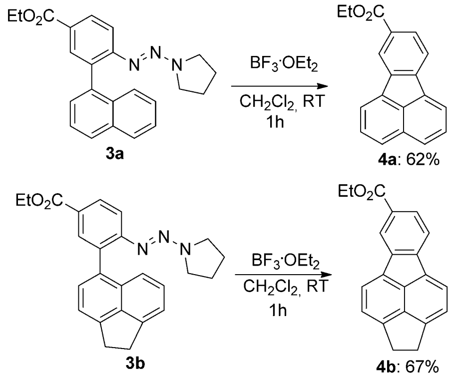
Entry	Substrate	Product	Yield [%]	Entry	Substrate	Product	Yield [%]
							
1[b]	**1a**: R = CO$_2$Et	**2a**: R = CO$_2$Et	77	10	**1j**: R = CO$_2$Et	**2j**: R = CO$_2$Et	84
2[b]	**1b**: R = CN	**2b**: R = CN	65	11	**1k**: R = CH$_3$	**2k**: R = CH$_3$	91
3	**1c**: R = CH$_3$	**2c**: R = CH$_3$	64				
							
4[b]	**1d**: R = CO$_2$Et	**2d**: R = CO$_2$Et	91	12	**1l**	**2l**	53
5[b]	**1e**: R = CN	**2e**: R = CN	79				
6	**1f**: R = CH$_3$	**2f**: R = CH$_3$	88				
							
7	**1g**: R = CO$_2$Et	**2g**: R = CO$_2$Et	88	13	**1m**	**2m**	73
8	**1h**: R = CH$_3$	**2h**: R = CH$_3$	66				
							
9	**1i**	**2i**	55	14	**1n**: R = CO$_2$Et	**2n**: R = CO$_2$Et	82
				15	**1o**: R = CH$_3$	**2o**: R = CH$_3$	79

[a] Reaction conditions: aryltriazene (0.5 mmol) and BF$_3$·OEt$_2$ (1.0 mmol) in CH$_2$Cl$_2$ (20 mL) for 30 min at room temperature. [b] Reaction run for 12 h at 40 °C.

regioselectively generate a range of functionalized polycyclic architectures.

Initially, we treated biaryl triazene **1a** (Table 1) with BF$_3$·OEt$_2$ (2.0 equiv) in CH$_2$Cl$_2$ at room temperature overnight, it provided the desired cyclization product **2a** in 47 % yield. When we carried out the reaction in CH$_2$Cl$_2$ under reflux, the yield increased to 77 %. The scope and limitations of this Lewis-acid-mediated Friedel-Crafts annulation process were examined using various biaryl triazenes. This annulation process can be extended to substrates bearing both electron-withdrawing groups (EWG) and electron-donating groups (EDG). The OCH$_3$-substituted biaryl triazene substrates (**1d–h**) are often produced in high yields in a short time, since the electron-rich aromatic rings serve as a nucleophile to attack the triazene aryl moiety; however, with CO$_2$Et-substituted (**1a–c**) aryl groups, the yield decreased. EWGs, such as CO$_2$Et (**1a–c**) and CN (**1d–e**), as substituents on triazene moiety retarded the cyclization rate and reduced the yields. However, prolonging the reaction time and elevating the reaction temperature increased the yields (**1a–b**, **1d–e**). The heteroatom-containing substrate **1i** also reacts well to afford the anticipated annulation compound **2i** in 55 % yield. A number of heteroatom-containing substrates, including benzofurans (**1j–m**) and indoles (**1n–o**), have also been employed in this annulation process and all afforded polycyclic materials successfully (**2j–o**) in 53–91 % yields.

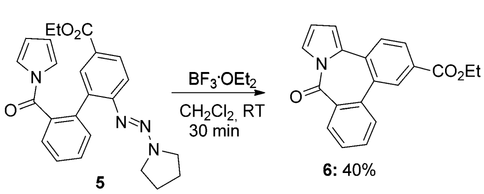
Owing to their utilization as synthetic precursors of coannulenes and as model fluorescent compounds for their high emission efficiency, the preparation of functionalized fluoranthenes has been valuable.[17] Our arylation cyclization reaction can be extended to prepare functionalized fluoranthenes. After treating aryl triazenes **3a** and **3b** with BF$_3$·OEt$_2$,



Scheme 2. Formation of fluoranthene derivatives **4a** and **4b**.

fluoranthenes **4a** and **4b** were generated in 62% and 67% yield, respectively (Scheme 2).

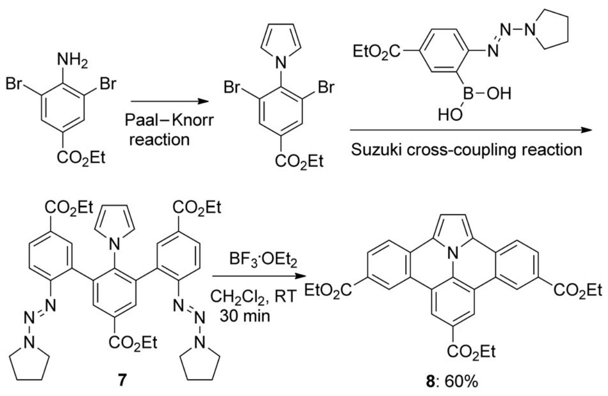
Seven-membered ring compounds are often difficult to access by classical routes. Recently, Greaney and Pintori[18] reported an intramolecular oxidative C–H coupling for medium-ring synthesis using an indole system catalyzed by [Pd(OAc)$_2$], however, three equivalents of [Cu(OAc)$_2$] was used. Considering this problem, we tried to adjust our metal-free intramolecular arylation method to generate seven-membered rings. After treatment of aryl triazene **5** with BF$_3$·OEt$_2$ in CH$_2$Cl$_2$ at room temperature for 30 min, the annulated seven-membered ring heterocyclic compound **6** was obtained in 40% yield (Scheme 3).



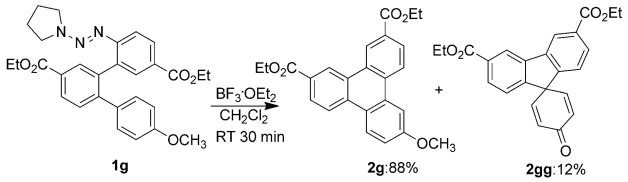
Scheme 3. Synthesis of annulated seven-membered ring heterocyclic compound **6**.

As hetero-π-conjugated molecules show dramatically different optical and electronic properties, we also tried to expand our reaction to construct polycyclic frameworks with pyrrole. Upon treatment of aryl triazene **7**, which was easily synthesized from 4-amino-3,5-dibromo-benzoic acid ethyl ester by a Paal–Knorr condensation and a Suzuki cross-coupling reaction, with BF$_3$·OEt$_2$ in CH$_2$Cl$_2$ at room temperature for 30 min, the double cyclization compound **8** (with the common name ullazine[19]) was obtained in 60% yield (Scheme 4).

To explore the reaction mechanism for the synthesis of PAHs, the following control experiments were performed under the standard reaction conditions. When treated the substrate **1g** with BF$_3$·OEt$_2$ in CH$_2$Cl$_2$, the reaction proceeded well and the desired compound **2g** was obtained in 88% yield, along with the by-product **2gg** in 12% yield (Scheme 5). When (2,2,6,6-Tetramethyl-piperidin-1-yl)oxyl (TEMPO), 1,1-diphenylethylene, or 2,6-di-*tert*-butyl-4-methylphenol (BHT), all of which are known to be effective radical scavengers,[20] were added to the reaction mixture, the desired compound **2g** was formed in 88–95% yield, but the by-product **2gg** was slightly decreased to 1–2% yield (Figure 1). In this reaction, the initial interaction between the terminal nitrogen atom of the triazene and the Lewis acid generates a diazonium salt[21] which decomposes through aryl cations and aryl radicals. This result implies that the desired product **2g** could form through an aryl cation mechanism, whereas by-product **2gg** could form through a radical pathway.



Scheme 4. Synthesis of πconjugated heterocyclic compound **8**.



Scheme 5. Investigation of the reaction mechanism.

In summary, we have developed a mild Friedel-Crafts intramolecular arylation approach to the regioselective synthesis of unsymmetrical and functionalized polycyclic aro-

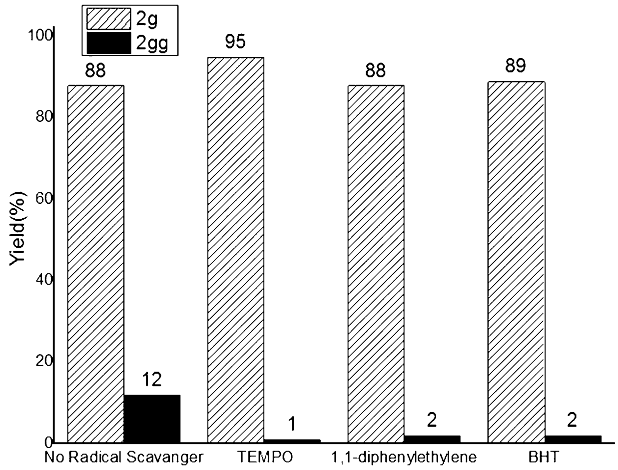


Figure 1. Influence of different radical scavengers. Reaction conditions: **1g** (0.5 mmol), BF$_3$·OEt$_2$ (1.0 mmol) and radical scavenger (0.5 mmol) in CH$_2$Cl$_2$ (20 mL) for 30 min at room temperature. Yields shown are of isolated products after chromatography. BHT = 2,6-di-*tert*-butyl-4-methylphenol, TEMPO = (2,2,6,6-Tetramethyl-piperidin-1-yl)oxyl.

matic hydrocarbons (PAHs) in good to excellent yields. These reactions are carried out under mild conditions with good tolerance for a variety of functional groups. Mechanistic investigations indicate that the reaction involves a highly activated phenyl cation intermediate. Further investigations into the reaction mechanism and synthetic applications are underway.

Experimental Section

Aryltriazene **1g** (0.5 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (20 mL), the solution was stirred at room temperature, and then $BF_3 \cdot OEt_2$ (127 μL, 2.0 equiv) was added dropwise. The mixture was stirred for 30 min and monitored by thin layer chromatography. Upon completion, saturated $NaHCO_3$ solution (2 mL) was added. The resulting mixture was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4, concentrated under reduced pressure and purified by silica gel chromatography with CH_2Cl_2 as eluent to give **2g** in 88 % yield and **2gg** in 12 % yield.

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Keywords: annulation · aryl triazenes · fluoranthenes · Friedel-Crafts arylation · polycycles

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