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Iodoarylation Reactions of Allenes: Inter- and Intramolecular Processes

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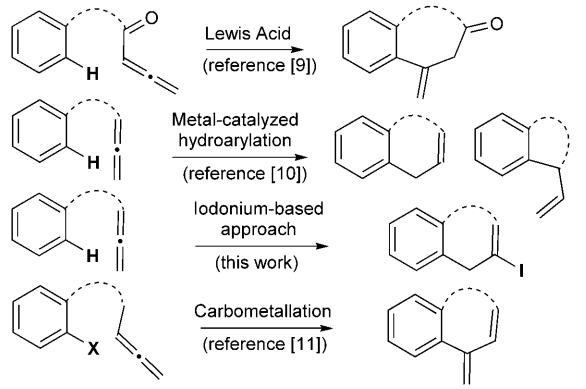
Polar addition reactions to allenes are well established and various processes involving this mechanistic pathway are known.[1,2] The reaction of arenes with electrophiles is a conceptually powerful method to functionalize C−H bonds.[3] Therefore, the feasibility of using carbon-based electrophiles, in reactions with arenes, was soon recognized as an entry for C−C bond formation. The Friedel–Crafts alkylation of arenes with alkenes is a relevant example.[4] Nevertheless, the related alkenylation reaction involving alkynes was more sluggishly developed and only recent advances involving metal-catalyzed transformations have made this target practicable.[5,6] The reaction of arenes with the transitory species generated upon interaction of iodonium ions with alkenes[7] or alkynes[8] represents a powerful route for preparing cyclic compounds involving related C−C bond-forming processes. Moreover, examples of Friedel–Crafts arylation reactions of allenes are rare.[9] Recent advances involve formally related processes using precious metal catalysts and are mainly intramolecular transformations.[10]

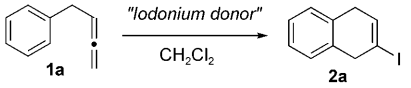
Herein, we report the first solid evidence on the use of iodonium ions as the trigger for an unprecedented β iodoallylation of a C−H bond of an arene by reaction with an allene (Scheme 1). Both, intra- and intermolecular processes are presented. The iodonium approach would complement the requirements of the powerful carbometallation reaction of allenes.[11] The intermolecular process requires a substituted arene, whereas in the intramolecular process the assembled skeleton is endowed with further functionality.[12] Interestingly, the application of this technology to ring elaboration enables a direct entry into the 2-iodo-1,4-dihydronaphthalene core, an elusive and valuable building block for cross-coupling chemistry that will also be highlighted.



Scheme 1. Arene addition reactions across allenes.

The iodonium-promoted carbocyclization was first tested on 2,3-butadienyl benzene (**1a**), a demanding model substrate considering that the participation of an electronically activated arene is mandatory in most allene hydroarylation reactions.[10] Several iodinating reagents were tested in an effort to synthesize 2-iodo-1,4-dihydronaphthalene (**2a**) through a straightforward iodoarylation strategy. Some key experiments are outlined in Table 1.

Table 1. Iodoarylation of **1a**: screening for useful iodonium donors.[a]



Entry	Iodinating reagent	T [°C]	t [min]	Yield **2a**[b] [%]
1	ICl	−80	25	–[c]
2	I_2	RT	20	–[d]
3	NIS/TfOH	−80	30	–[e]
4	IPy_2BF_4/HBF_4	−90	20	70[f]

[a] **1a** (0.1 M, 1 mmol scale); **1a**/iodinating agent (1:1). [b] Yield of the isolated products. [c] ICl–allene adducts. [d] I_2 addition to the terminal allene bond. [e] Acetone used as solvent, **1a**/TfOH (1:1); 50% of **1a** recovered from a complex mixture. [f] HBF_4 added (1 equiv, 54% in Et_2O); monitoring by TLC showed instantaneous disappearance of **1a**.

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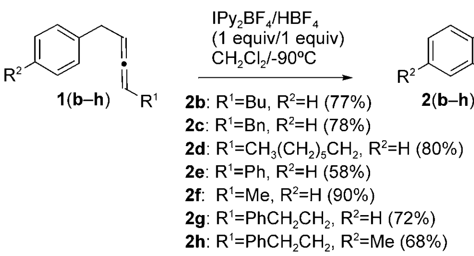
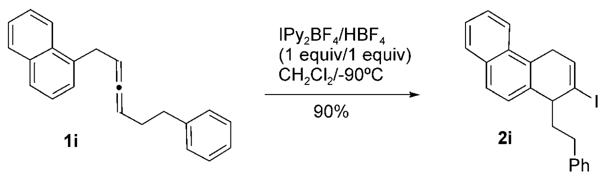
The IPy_2BF_4 reagent (Py = pyridine) acted as a genuine iodonium donor to achieve the desired ring-closing step.[13] This cyclization requires prior treatment of the iodinating agent with HBF_4 (1 equiv) to preclude pyridine incorporation. Performing the reaction at low temperature avoids competitive side processes and enables a fast cyclization.[14] Other iodinating agents did not promote the cyclization of **1a**. Instead, the products of facile addition reactions were observed. These adducts are formed upon capture of the intermediate iodonium ions by an external nucleophile, resulting from activation of **1a** by a true source of electrophilic iodine. Formation of the adducts could not be prevented, even when conducting the cyclization at lower temperatures. Nonetheless, the influence that the iodonium source may have over the reaction outcome was further tested in cyclization reactions employing **1b** and **1c**. The cyclizations accomplished by using IPy_2BF_4 are depicted in Scheme 2. The reaction of **1b** with ICl gave rise to a complex mixture, which included **2b**. Interestingly, *N*-iodosuccinimide (NIS) selectively gave the cyclization product **2b** in 85 % yield.[15] In contrast, several attempts to cyclize **1c** by using both reagents were ineffective. In general, IPy_2BF_4 provided a robust method for the synthesis of the target 1,4-dihydronaphthalene core and was systematically used in related cyclizations (Scheme 2).[16]



Scheme 2. Iodoarylation of 3-substituted-2,3-butadienylbenzenes for instant entry to derivatives of the 2-iodo-1,4-dihydronaphthalene core.

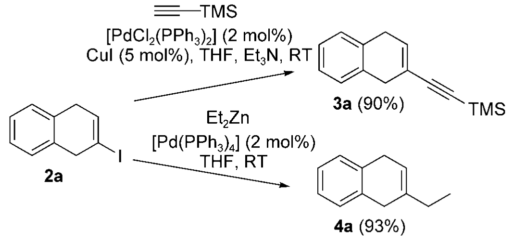
As depicted, allenes with various C substituents yielded the desired iodinated dihydronaphthalene scaffold. The lower isolated yield for the substrate with the phenyl substituent, **2e**, reflects its lack of stability to the reaction conditions and, particularly, to the purification step. The results outlined in Scheme 2 were obtained from reactions routinely conducted by employing 1 mmol of **1**; nonetheless, some reactions were also scaled up. As a result, compound **2a** was prepared in comparable yield when 30 mmol of **1a** were used.[17] All of the reported cyclizations led selectively to the formation of a six-membered ring. The reaction of **1g** provides a striking example of this feature. In this case, upon activation of the allene at the central carbon, the reaction might progress by ring-closing processes leading to the formation of either a six- or five-membered ring. Only the former pathway was observed. The regiochemistry of the iodonium-promoted cyclization is complementary to that of the carbopalladation of 1,2-dienes.[18]

Interestingly, other partially hydrogenated scaffolds derived from related aromatic hydrocarbons can be accessed by this methodology. Thus, the intramolecular allene iodoarylation strategy also enables the easy construction of the elusive 2-iodo-1,4-dihydrophenanthrene framework featured in **2i** (Scheme 3).[19]



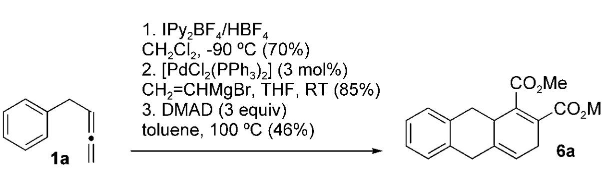
Scheme 3. Access to 2-iodo-1,4-dihydrophenanthrene derivatives by applying an iodoarylation reaction.

By design, all of the assembled carbocycles feature an alkenyl iodide functionality[20] that can be exploited for the fast introduction of molecular complexity. Significant transformations of **2a** by Sonogashira or Negishi cross-coupling reactions, leading to **3a** and **4a** are depicted in Scheme 4.[21] These simple derivatives are not accessible by using a Birch reduction of the parent arenes.



Scheme 4. Rapid molecular diversification from allenes: iodonium-promoted cyclization/metal-catalyzed cross-coupling strategy.

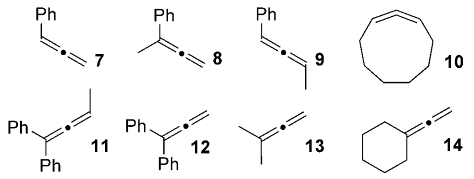
The Kumada cross-coupling reaction with vinylmagnesium bromide gave 2-vinyl-1,4-dihydronaphthalene (**5a**) in 85 % yield as a new compound that was further elaborated to give the polycyclic skeleton of **6a** upon heating with dimethyl acetylenedicarboxylate (DMAD). The overall sequence gave practical access to a rare unsaturated motif (Scheme 5).



Scheme 5. Construction of polycyclic systems by allene iodoarylation.

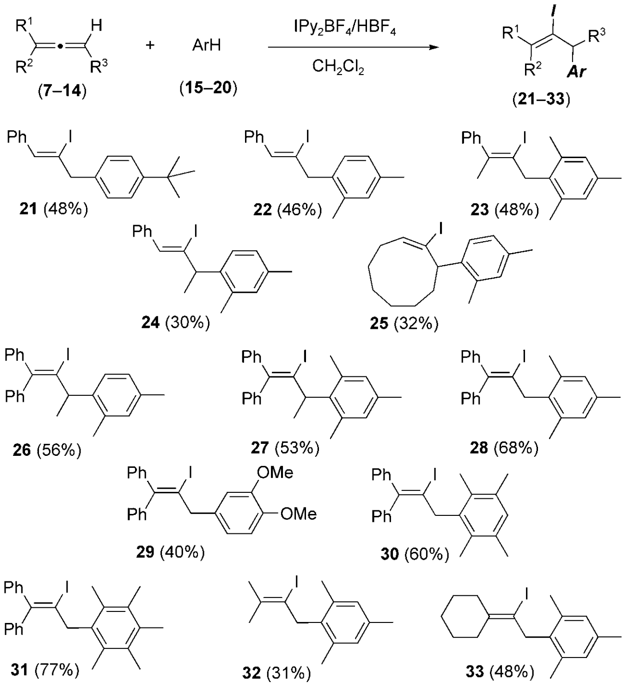
The cyclization leading to the formation of **2** from **1** could be reasonably explained by assuming an initial interaction of the allene with the iodonium ion. Bonding the electrophile to the central carbon atom of the allene would lead to the formation of an electron-deficient species stabilized by the neighboring iodine atom.[22] This would render the terminal carbon atom of the allene electrophilic, allowing a subsequent Friedel–Crafts-like process to take place. The electrophilic nature of this ring-closing step would favor the formation of a six-membered ring, as is observed. For **1g**, the lack of formation of the five-membered ring product supports this view, as opposed to a radical pathway.

The intermolecular hydroarylation reaction of allenes is a demanding process and has scarcely been reported. Recent studies focusing on the usefulness of different catalytic systems report timely and synthetically valuable alternatives.[23] We decided to try to develop another alternative based on an intermolecular iodoarylation reaction of allenes. Our study began by exploring the dependence of the process on the electronic activation of the arene and on the degree of substitution of the allene. Regarding the latter characteristic, the process was found to tolerate a wide set of simple model allenes, ranging from mono- up to trisubstituted allenes (**7**–**14**).



Moderately activated arenes are needed to furnish the desired adducts. Benzene itself fails to add efficiently across 1-phenyl-1,2-propadiene (**7**). However, arenes, such as 4-*tert*-butylbenzene (**15**) or 1,3-dimethylbenzene (**16**) successfully reacted with the monosubstituted allene **7** to give compounds **21** and **22**, respectively, in moderate yields (Scheme 6). Two sets of conditions (method A or B) were established in an attempt to influence the process.[24] Thus, by using appropriate experimental conditions, more electron-rich arenes, such as 1,2-dimethoxybenzene (**18**) or pentamethylbenzene (**20**), could take part in this process (see compounds **29** and **31**). Unfortunately 1*H*-indole failed to provide adducts under related conditions.

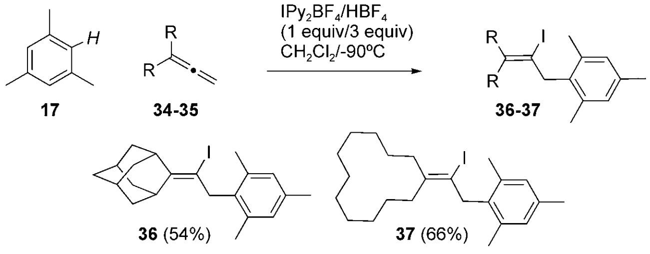
For all compounds depicted in Scheme 6, the reactions were conducted by using an excess of the arene with respect to the allene (3:1 molar ratio). Conventional TLC is useful for monitoring the reaction progress. It shows the disappearance of the parent allene, typically in the range of 30–90 min, with the slower reaction corresponding to the trisubstituted allene **11**. For the intermolecular reaction, two synthetic constraints were identified. Thus, for the assayed 1,3-disubstituted allenes (**9** and **10**), 1,2-iodofluorination occurs as a competitive process, hampering the yield of the corresponding iodoarylation product. Depending on the nature of the allene, aromatic iodination might also become a limiting process. As for the intermolecular hydroarylation reaction of allenes, the iodoarylation process also requires moderately activated arenes. However, the compatibility of the iodoarylation approach with the allene substitution pattern is slightly superior to that found in alternative electrophilic addition reactions of arenes to allenes promoted by cationic gold species. Interestingly, as a rule, this C–C/C–I bond-forming approach gives the addition products as single isomers.[25]



Scheme 6. Intermolecular allene iodoarylation: exploratory studies.

This iodonium-promoted C–C bond-forming process can be rationalized in terms of an electrophilic aromatic substitution reaction. Although mechanistically unrelated, the iodoarylation of allenes reported herein could be formally viewed as a method to synthesize the products that result from an arene C–H activation, followed by insertion to the allene and trapping with iodine. Overall, this iodonium approach lacks precedent and gives β-iodoallylated arenes in a straightforward manner. As a result, this methodology could be a key step in a direct approach to the preparation of a class of tetrasubstituted alkenes featuring a distinctive C–I bond available for subsequent and selective functionalization (Scheme 7).

In summary, intra- and intermolecular pathways enabling a new arylation reaction of allenes have been presented.



Scheme 7. Straightforward assembly of hybrid cycloalkane–arene scaffolds using a novel C-H arene functionalization approach.

This approach makes the preparation of some, as yet unknown, basic scaffolds possible. It is foreseeable that this methodology may be applicable to the assembly of other elusive molecular frameworks.

Experimental Section

Typical procedure (synthesis of 2a): A 54% solution of HBF_4 in diethyl ether (1 equiv, 0.14 mL; commercially available) was added to a stirred solution of IPy_2BF_4 (1 equiv, 0.372 g) in CH_2Cl_2 (8 mL) at −30°C. After stirring for 10 min, the mixture was cooled to −90°C and a solution of **1a** (1 mmol, 0.130 g) in CH_2Cl_2 (2 mL) was added. Once the starting allene had disappeared (typically after a few minutes as monitored by TLC), the reaction was quenched by addition of an aqueous solution of $Na_2S_2O_3$ (5%) and warmed to room temperature. After extraction with CH_2Cl_2 the mixture was consecutively washed with a 5% aqueous solution of $Na_2S_2O_3$ and a 1 N aqueous solution of HCl, the organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness. Purification of the residue by column chromatography on silica gel (hexane as eluent) afforded **2a** as a colorless oil (0.179 g, 70%).

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Keywords: allenes · arenes · cyclization · electrophilic substitution · iodination

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[14] Addition of lower amounts of acid gave a poorer yield of **2a**, whereas no significant differences were found when up to three equivalents of acid were added. When the reaction was conducted at −70°C, compound **2a** was isolated in 60% yield. Increasing the temperature enables iodofluorination reactions of the allene to occur.

[15] The reaction of NIS and TfOH (1 equiv) was conducted in acetone. TLC showed the disappearance of **1b** after reaction for 6 min at −80°C; compound **2b** was isolated after chromatographic column in 85% yield. For the reaction of **1b** with ICl, standard chromatographic purification of the crude mixture did not render pure samples of **2b**. Therefore, although an isolated yield cannot be reported, its formation is estimated in the 50% range.

[16] For experimental details and characterization data, see the Supporting Information. Compounds **2–6**, **21–33**, **36**, and **37** were characterized by NMR spectroscopy and MS data. New compounds gave satisfactory elemental analysis and/or HRMS data according to their structures.

[17] Reaction conducted at a higher concentration (0.5 M).

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[24] Method A (synthesis of **21**–**27**): allene (1 equiv), $\mathrm{IPy_2BF_4}$ (1 equiv), $\mathrm{HFB_4}$ (0.8 equiv), $\mathrm{CH_2Cl_2}$, −40 °C. Method B (synthesis of **28**–**33** and **36**–**37**): allene (1 equiv), $\mathrm{IPy_2BF_4}$ (1 equiv), $\mathrm{HFB_4}$ (3 equiv), $\mathrm{CH_2Cl_2}$, −90 °C.

[25] NMR spectroscopy analysis of crude reaction mixtures showed the formation of the addition products as a single stereoisomer, together with an excess of the arene and some iodoarene. Exceptions to this trend (not depicted in Scheme 6): 1,2-dimethylbenzene and 1,1-diphenyl-1,2-propadiene gave (method B) an inseparable mixture of 1,2,4- and 1,2,3-iodoarylated isomers, (41 %, 2:1 ratio, respectively). Iodonium-promoted addition of 1,3,5-trimethylbenzene to 1-phenyl-1,2-propadiene occurs (method A) with low selectivity (51 % combined yield). Addition to the terminal double bond mainly takes place to give a 5:1 mixture of *Z* and *E* isomers, respectively. Trace amounts of addition to the internal bond were detected in the crude mixture.

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