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Iodine-Initiated Domino Reaction of Hepta-1,2-dien-6-yn-4-ols and Brønsted Acid Promoted Cyclization of Hepta-1,2,6-trien-4-ols Leading to Functionalized Benzenes

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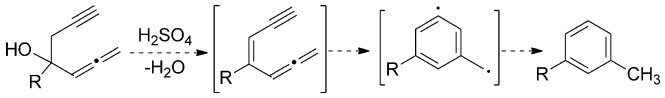
Functionalized benzenes, in particular, carbonyl- or iodo-substituted benzenes, are attractive synthetic targets as they are not only commmon structural units in natural products and pharmaceuticals, but also among the most commonly used precursors in organic synthesis.[1] While direct functionalization of aromatic starting materials is often used to prepare the required functionalized benzenes, construction of aromatic rings from the easily obtainable acyclic units constitutes another efficient way for this purpose.[2]

Cycloaromatization of enyne–allenes through a radical intermediate, known as the Myers–Saito cyclization, is documented as an efficient method for the preparation of benzenoid compounds.[3] However, the utility of this strategy is compromised as the enyne–allene precursors are usually obtained through multi-step processes that employ expensive catalysts and reagents, or generated in situ through noble transition-metal-catalyzed sigmatropic rearrangement of propargylic acetates or propargyl vinyl ethers.[3,4]

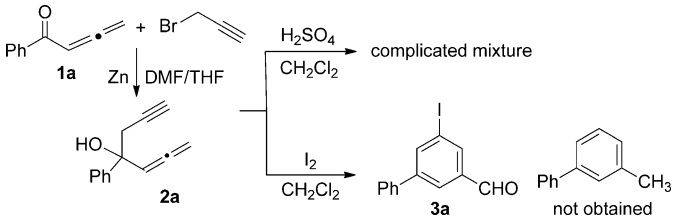
In our recent study on the chemistry of allene derivatives,[5] we have developed a synthetic approach toward 2*H*-pyran-2-ones through the tandem reaction of 3-hydroxyhexa-4,5-allenic esters.[5c] The reaction is thought to be initiated by an acid-promoted dehydration of the tertiary alcohol followed by hydration of the allene moiety and an intramolecular esterification of the in situ formed enol unit.

In light of the high efficiency and mild conditions involved in the above-mentioned process, we hypothesized that an acidic promoter might trigger the Myers–Saito process through dehydration of hepta-1,2-dien-6-yn-4-ol to give the required hepta-1,2,4-trien-6-yne. Subsequent cycloaromatization of the enyne–allene intermediate would afford a biradical intermediate, from which a *meta*-substituted toluene molecule is supposed to be formed (Scheme 1).



Scheme 1. Proposed cycloaromatization of hepta-1,2-dien-6-yn-4-ol.

To check the feasibility of the above proposal, 4-phenylhepta-1,2-dien-6-yn-4-ol (**2a**)[6] was prepared from 1-phenylbuta-2,3-dien-1-one (**1a**) and propargyl bromide under the promotion of zinc and was then treated with H_2SO_4 in CH_2Cl_2 (Scheme 2) under reflux. To our disappointment, the



Scheme 2. Unexpected formation of **3a** from **2a**.

reaction afforded a complicated mixture of compounds, instead of the expected 3-methylbiphenyl. Based on the observations made by Hibbert et al. that iodine is highly efficient in promoting the dehydration of tertiary alcohols,[7] **2a** was then treated with I_2 (1 equiv) in CH_2Cl_2 at reflux for 10 h. Surprisingly, 5-iodo-biphenyl-3-carbaldehyde (**3a**), instead of the expected 3-methylbiphenyl, was obtained in a yield of 36% (Scheme 2).

The unexpected formation of **3a** turns out to be a synthetically useful and mechanistically attractive finding as it not only reveals a novel iodine-initiated cyclization, but also provides an unprecedented protocol for the one-pot introduction of two valuable functional groups, namely, iodo and formyl, onto the benzene ring along with the construction of the benzenoid core.

To develop the above reaction into a new synthetic pathway toward iodobenzaldehyde, we proceeded to optimize the reaction conditions. The effect of solvent on this tandem reaction was studied first. It turned out that CH_3CN gave the best results (Table 1, entries 1–6). Different reaction temperatures and amounts of iodine were also tested

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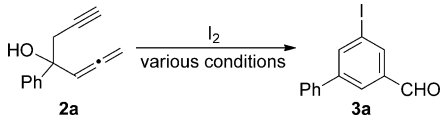
Table 1. Optimization studies for the synthesis of **3a**.[a]



2a **3a**

Entry	Solvent	I_2 [equiv]	T [°C]	t [h]	Yield [%][b]
1	CH_2Cl_2	1	reflux	10	36
2	Toluene	1	60	10	40
3	DMF	1	60	10	28
4	CH_3CN	1	60	10	60
5	EtOH	1	60	10	trace
6	H_2O	1	60	10	25
7	CH_3CN	0.2	60	12	26
8	CH_3CN	0.5	60	12	51
9	CH_3CN	2	60	5	61
10	CH_3CN	1	r.t.	10	trace
11	CH_3CN	1	40	10	43
12	CH_3CN	1	reflux	10	75

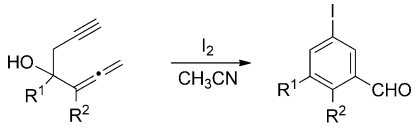
[a] Reaction conditions: **2a** (0.5 mmol), solvent (5 mL); [b] Yield of isolated product.

(Table 1, entries 7–12). After exhaustive studies, the optimal reaction conditions were identified as follows: treating **2a** with 1 equivalent of I_2 in CH_3CN at reflux under air for 10 h afforded **3a** in 75% yield.

With the optimized conditions in hand, we screened a range of hepta-1,2-dien-6-yn-4-ols (**2**) to probe the scope of the present reaction (Table 2). It turns out that substrates derived from aryl-substituted allenic ketones with various substituents on the aryl ring undergo this reaction smoothly in good to excellent yields (Table 2, entries 1–15). Various functional groups, such as electron-rich methoxy and electron-deficient cyano groups, are well tolerated under the reaction conditions. Interestingly, using substrates with a methyl or ethyl group at the internal position of the allene moiety, also results in a smooth transformation to afford the corresponding 3-iodobenzaldehydes efficiently (Table 2, entries 16–21). Moreover, the reaction is also found to be compatible with substrates prepared from benzyl- or phenylethyl-substituted allenic ketones, although the yields are somewhat lower (Table 2, entries 22–24). The molecular structure of the representative product **3f** was determined by X-ray crystallographic analysis.[8]

Based on the above observations and related literature procedures, it is reasoned that the role played by I_2 in this tandem process is not only promoting the dehydration of the tertiary alcohol, but also initiating the subsequent cyclization of the in situ formed enyne–allene intermediate. Therefore, a plausible pathway for the formation of iodobenzaldehyde (**3**) is proposed, as shown in Scheme 3. Initially, I_2-promoted dehydration of **2** through a carbocation (**I**) affords an enyne–allene intermediate (**II**).[9] Subsequently, coordination of I_2 to the carbon–carbon triple bond in **II** affords an iodonium intermediate (**III**), which then undergoes a nucleophilic attack on the allenyl moiety to give a benzyl cation (**IV**).[10] Trapping of **IV** by iodide would afford 3-iodobenzyl iodide (**V**).[11] Oxidation of **V** by air affords **3** as the final product.[12]

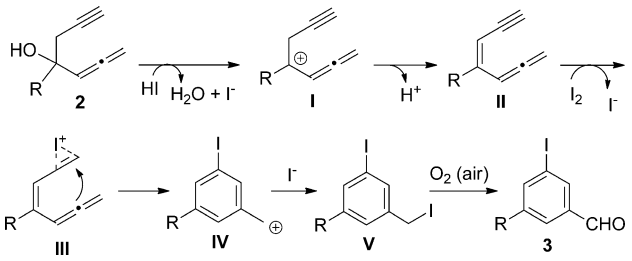
Table 2. Synthesis of iodobenzaldehydes (**3**).[a]



2 **3**

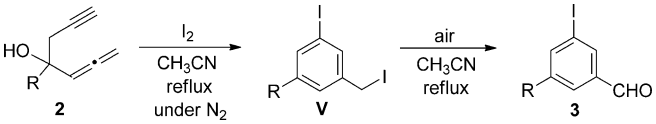
Entry	R^1	R^2	**3**	Yield [%][b]
1	Ph	H	**3a**	75
2	*p*-CH_3O-C_6H_4	H	**3b**	62
3	*p*-CH_3-C_6H_4	H	**3c**	64
4	*p*-F-C_6H_4	H	**3d**	81
5	*p*-Cl-C_6H_4	H	**3e**	80
6	*p*-Br-C_6H_4	H	**3f**	77
7	*p*-NC-C_6H_4	H	**3g**	82
8	*m*-CH_3-C_6H_4	H	**3h**	66
9	*m*-F-C_6H_4	H	**3i**	72
10	*m*-Cl-C_6H_4	H	**3j**	70
11	*m*-Br-C_6H_4	H	**3k**	74
12	*o*-F-C_6H_4	H	**3l**	66
13	*o*-Cl-C_6H_4	H	**3m**	65
14	*m*,*p*-di-CH_3O-C_6H_3	H	**3n**	68
15	*2-naphthyl*	**H**	**3o**	70
16	*p*-CH_3O-C_6H_4	CH_3	**3p**	65
17	*p*-CH_3-C_6H_4	CH_3	**3q**	59
18	*p*-Br-C_6H_4	CH_3	**3r**	63
19	*p*-Cl-C_6H_4	CH_3	**3s**	64
20	*m*-Cl-C_6H_4	CH_3	**3t**	62
21	*o*-Cl-C_6H_4	C_2H_5	**3u**	58
22	$PhCH_2$	H	**3v**	48
23	$PhCH_2$	CH_3	**3w**	45
24	$PhCH_2CH_2$	H	**3x**	38

[a] Reaction conditions: **2** (1 mmol), I_2 (1 mmol), CH_3CN (5 mL), reflux, 10 h; [b] Yield of isolated product.



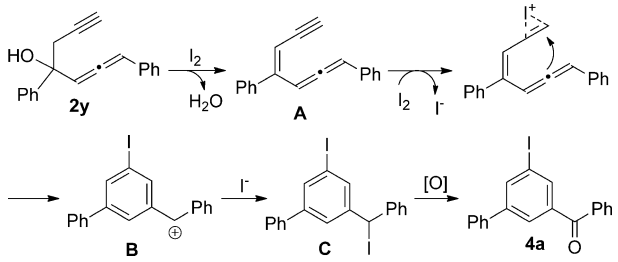
Scheme 3. Plausible pathway for the formation of **3** from **2**.

The proposed mechanism for the formation of **3** is supported by the following facts: 1) when **2** was treated with I_2 under a nitrogen atmosphere, the reaction mainly gave 3-iodobenzyl iodide (**V**) instead of **3**; 2) 3-iodobenzyl iodide (**V**) could be isolated from the reaction mixture and its structure was confirmed by X-ray diffraction analysis;[13] 3) when the solution of **V** in CH_3CN was refluxed under air for several hours, **V** could be transformed into **3** in high efficiency (Scheme 4).



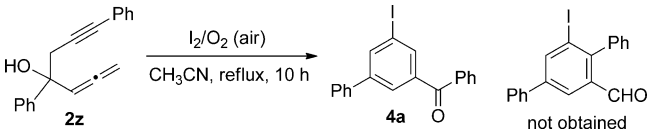
Scheme 4. Formation and transformation of intermediate **V**.

To further explore the scope of the above reaction, 1,4-diphenylhepta-1,2-dien-6-yn-4-ol (**2y**), bearing a phenyl group at the terminal position of the allene moiety, was employed. It turned out that an iodobenzophenone, (5-iodobiphenyl-3-yl)(phenyl) methanone (**4a**), could be obtained in a yield of 42%. **4a** is supposed to be formed through an allene–enyne (**A**) and a diphenyl methyl cation (**B**), as shown in Scheme 5.



Scheme 5. Plausible pathway for the formation of **4a** from **2y**.

In the following study, the reaction of 4,7-diphenylhepta-1,2-dien-6-yn-4-ol (**2z**), with a phenyl group at the terminal position of the alkyne moiety, was also investigated. Upon treatment with iodine, to our surprise, it still gave **4a** rather than the expected 3-iodo-2,5-diphenylbenzaldehyde (Scheme 6).

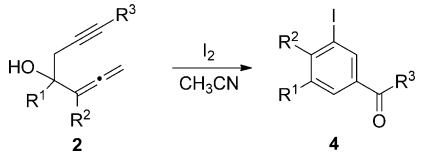


Scheme 6. Unexpected formation of **4a** from **2z**.

This interesting result might be explained by a plausible pathway as shown in Scheme 7. It is assumed that the internal alkynyl moiety of enyne–allene **D** is less reactive than the allenic moiety towards iodine. Therefore, the cyclization is initiated by the coordination of iodine to allene rather than to the alkyne. Subsequent cyclization affords a diphenyl methyl cation intermediate (**B**), which is far more stable than the proposed benzyl cation (**E**) that is required for the formation of 3-iodo-2,5-diphenylbenzaldehyde owing to both electronic and steric reasons. As a result, instead of going through intermediate **E** to give 3-iodo-2,5-diphenyl benzaldehyde, under the reaction conditions, **2z** would undergo a tandem process via intermediate **B** to afford **4a**.

Next, a series of hepta-1,2-dien-6-yn-4-ols with a phenyl, methyl, or ethyl group at the terminal position of the triple bond were prepared and treated with I_2 in CH_3CN with the aim to develop the reaction shown in Scheme 6 into a general synthetic method toward iodoaryl ketones. It turned out that all the substrates studied underwent the tandem process smoothly to give the corresponding iodo-substituted diaryl ketones (Table 3, entries 1 and 2), aryl methyl ketones

Table 3. Synthesis of iodoarylketones (**4**).[a]

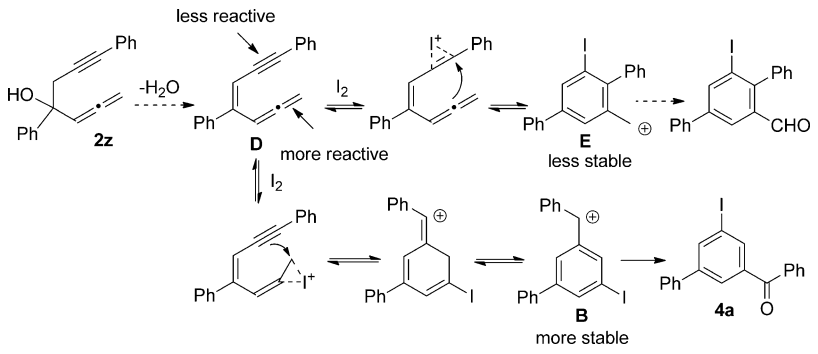


Entry	R^1	R^2	R^3	**4**	Yield [%][b]
1	C_6H_5	H	C_6H_5	**4a**	68
2	*p*-CF_3-C_6H_4	H	C_6H_5	**4b**	70
3	C_6H_5	H	CH_3	**4c**	52
4	*m*-Cl-C_6H_4	H	CH_3	**4d**	55
5	*m*-Br-C_6H_4	H	CH_3	**4e**	50
6	*p*-Cl-C_6H_4	H	CH_3	**4f**	58
7	*p*-Br-C_6H_4	H	CH_3	**4g**	62
8	*p*-CH_3-C_6H_4	H	CH_3	**4h**	51
9	*p*-CF_3-C_6H_4	H	CH_3	**4i**	63
10	*o*-Cl-C_6H_4	H	C_2H_5	**4j**	45
11	*p*-CF_3-C_6H_4	H	C_2H_5	**4k**	55
12	C_6H_5	CH_3	CH_3	**4l**	51

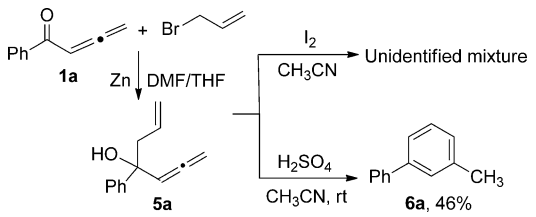
[a] Reaction conditions: **2** (0.5 mmol), I_2 (0.5 mmol), CH_3CN (5 mL), reflux, 10 h; [b] Yield of isolated product.

(Table 3, entries 3–9), as well as aryl ethyl ketones (Table 3, entries 10 and 11) in moderate to good yields. It is noted that the reaction is also compatible with substrates that bear a methyl group at the internal position of the allene moiety (Table 3, entry 12).

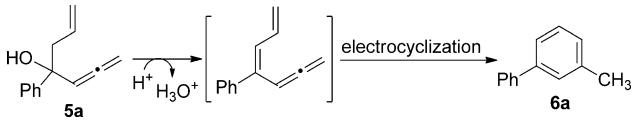
Having explored the reactivity of hepta-1,2-dien-6-yn-4-ol (**2**), our attention moved to its allyl counterpart, hepta-1,2,6-trien-4-ol (**5**). We found that 4-phenylhepta-1,2,6-trien-4-ol (**5a**) could be prepared through a zinc-promoted reaction of **1a** with allyl bromide; when treated with I_2 in CH_3CN, it gave an unidentifiable mixture of compounds. On the other hand, treatment of **5a** with H_2SO_4 in CH_3CN at room temperature for 2 h afforded 3-methylbiphenyl (**6a**) in a yield of 46% (Scheme 8).



Scheme 7. Plausible pathway for the formation of **4a** from **2z**.



Scheme 8. Formation of **6a** through H_2SO_4 promoted cyclization of **5a**.



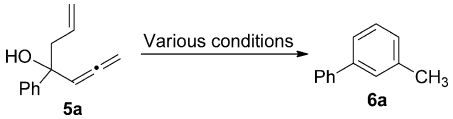
Scheme 9. Plausible pathway for the formation of **6a**.

Mechanistically, the formation of **6a** is thought to involve an electrocyclization process of a diene–allene intermediate, which must be formed in situ through an acid-promoted dehydration of **5a** (Scheme 9).

Pioneering works have proven that the 6π-electrocyclization of diene–allenes is an efficient protocol for the construction of the benzene ring.[14] However, the main challenge in employing this strategy to prepare substituted benzenes is how to obtain the required diene–allene intermediates. While isomerization of propargyl diene is an elegant approach toward diene–allenes,[15] dehydration of the readily available hepta-1,2,6-trien-4-ol (**5**) as described above provides another good solution to this problem.

Afterwards, the reaction of **5a** towards **6a** was optimized by employing different solvents and catalysts (Table 4). Initially, it was found that the solvent affects the outcome of this reaction significantly. Among the solvents studied, CH_2Cl_2 is the most effective. With CH_2Cl_2 as a medium, other Brønsted acids such as TsOH, CF_3COOH, and CCl_3COOH were also tried but they were less effective than H_2SO_4 in promoting this reaction. In summary of the optimization studies, **6a** could be obtained in 81 % yield when the reaction was carried out in CH_2Cl_2 at room temperature for 0.2 h in the presence of 1 equivalent of H_2SO_4 (Table 4, entry 5).

Table 4. Optimization studies for the formation of **6a**.[a]

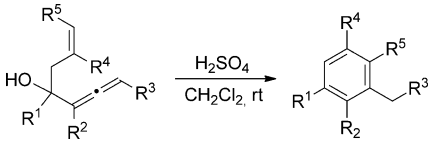


Entry	Acid	Solvent	*t* [h]	Yield [%][b]
1	H_2SO_4	CH_3CN	2	46
2	H_2SO_4	C_2H_5OH	2	trace
3	H_2SO_4	Et_2O	2	trace
4	H_2SO_4	THF	2	25
5	H_2SO_4	CH_2Cl_2	0.2	81
6	TsOH	CH_2Cl_2	5	35
7	CF_3CO_2H	CH_2Cl_2	5	45
8	CH_3CO_2H	CH_2Cl_2	5	trace
9	CCl_3CO_2H	CH_2Cl_2	5	30
10	H_2SO_4 (0.2 equiv)	CH_2Cl_2	6	22
11	H_2SO_4 (0.5 equiv)	CH_2Cl_2	6	54

[a] Reaction conditions: **5a** (0.5 mmol), solvent (5 mL), acid (0.5 mmol), rt; [b] Yield of isolated product.

Based on the above results, the scope and generality of the reaction that leads to **6** was studied. For most of the hepta-1,2,6-trien-4-ols (**5**) studied, the reactions proceeded smoothly to afford 1,3-disubstituted benzenes in good yields (Table 5, entries 1–16). It is noted that substrates with electron-deficient substituents on the phenyl ring usually give the corresponding products in higher yields (Table 5, entries 2–4, and 11–15) than those with electron-rich substituents (Table 5, entries 9, 10, and 16). 3-ethylbiphenyl was obtained by employing a substrate that posseses a methyl group at the terminal position of the allene moiety (Table 5, entry 17). Moreover, for substrates with a methyl group at the terminal or the inner position of the vinyl moiety, or at the internal position of the allene moiety, 1,3,4-, 1,3,5-, or 1,2,3-trisubstituted benzene derivatives could be synthesized with high efficiency (Table 5, entries 18–20), thus making this reaction a versatile pathway toward diversely substituted benzenes.

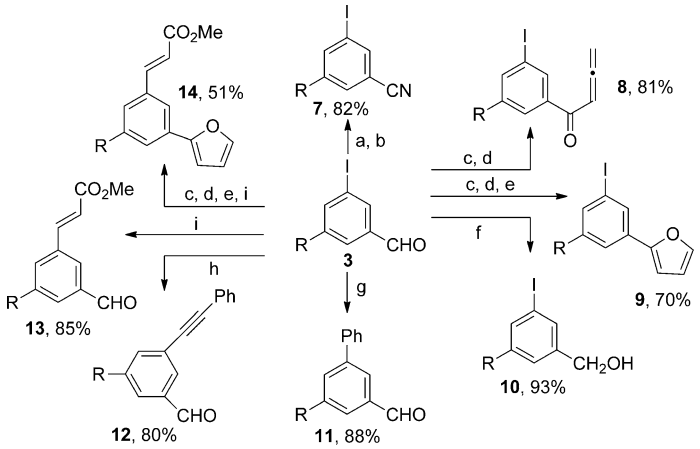
Table 5. Synthesis of substituted benzenes (**6**).[a]



Entry	R^1	R^2	R^3	R^4	R^5	**6**	Yield [%][b]
1	C_6H_5	H	H	H	H	**6a**	81
2	*o*-F-C_6H_4	H	H	H	H	**6b**	85
3	*o*-Cl-C_6H_4	H	H	H	H	**6c**	84
4	*o*-Br-C_6H_4	H	H	H	H	**6d**	82
5	*m*-CH_3-C_6H_4	H	H	H	H	**6e**	72
6	*m*-F-C_6H_4	H	H	H	H	**6f**	79
7	*m*-Cl-C_6H_4	H	H	H	H	**6g**	78
8	*m*-Br-C_6H_4	H	H	H	H	**6h**	75
9	*p*-CH_3O-C_6H_4	H	H	H	H	**6i**	45
10	*p*-CH_3-C_6H_4	H	H	H	H	**6j**	70
11	*p*-F-C_6H_4	H	H	H	H	**6k**	88
12	*p*-Cl-C_6H_4	H	H	H	H	**6l**	86
13	*p*-Br-C_6H_4	H	H	H	H	**6m**	85
14	*p*-NC-C_6H_4	H	H	H	H	**6n**	90
15	*p*-CF_3-C_6H_4	H	H	H	H	**6o**	86
16	2-naphthyl	H	H	H	H	**6p**	53
17	*p*-Cl-C_6H_4	H	CH_3	H	H	**6q**	83
18	*p*-CH_3-C_6H_4	H	H	CH_3	H	**6r**	68
19	C_6H_5	H	H	H	CH_3	**6s**	80
20	*o*-Br-C_6H_4	CH_3	H	H	H	**6t**	75

[a] Reaction conditions: **5** (1 mmol), H_2SO_4 (1 mmol), CH_2Cl_2 (5 mL), rt, 0.2 h; [b] Yield of isolated product.

Finally, the versatile transformation and valuable synthetic applications of iodobenzaldehyde (**3**) was explored and the results are demonstrated in Scheme 10. While keeping the iodo group intact, the carbonyl group could be conveniently transformed into a cyano, allenic ketone, furan, or alcohol unit. On the other hand, the iodo group could be used



Scheme 10. Versatile transformations and synthetic applications of **3**.[a,b] [a] R = C_6H_5, or 4-NCC_6H_4. [b] Reagents and conditions: a) $NH_2OH{\cdot}HCl$, NaOAc, THF/H_2O (10:3), rt, 1 h; b) $POCl_3$, CH_3CN, rt, 1 h; c) 3-bromoprop-1-yne, Zn, THF/DMF, rt, 0.5 h; d) Jones reagent, acetone, 0 °C, 5 min; e) $AgNO_3$, CH_3CN, reflux, 1 h; f) KBH_4, CH_3OH, rt, 1 h; g) $PhB(OH)_2$, $[Pd(PPh_3)_4]$, Na_2CO_3, toluene/CH_3OH (20:1), 100 °C, 9 h; h) Ethynyl benzene, $[PdCl_2(PPh_3)_2]$, CuI, NEt_3, CH_3CN, 30 °C, 16 h; i) Methyl acrylate, $Pd(OAc)_2$, PPh_3, NEt_3, DMF, 90 °C, 1 h. DMF = *N*,*N*-dimethylformamide.

as a useful handle for various coupling reactions to give biphenyl, diphenyl acetylene, or cinnamate in high efficiency. Moreover, both iodo and carbonyl groups could be elaborated to give 1,3,5-trifunctionalized benzenes.[16]

In summary, we have developed an efficient protocol for the preparation of iodobenzaldehydes and iodoaryl ketones through an iodine-promoted domino reaction of hepta-1,2-dien-6-yn-4-ols through the cyclization of the in situ formed enyne–allene intermediate. Compared with previous reports on the cyclization of enyne–allene, the present method not only provides a facile way to obtain the required enyne–allene intermediate, but also reveals an unprecedented concurrent introduction of both iodo and carbonyl groups onto the benzene ring as well as construction of the benzenoid core. In a further aspect, we also discovered an easy-to-perform synthetic pathway towards diversely substituted benzenes through a Brønsted acid promoted cascade reaction of hepta-1,2,6-trien-4-ols that featured a cyclization of the in situ formed diene–allene intermediate. With advantages such as readily available starting materials, mild reaction conditions, and diverse substitution pattern of products, the synthetic processes developed in this study are expected to be used as valuable alternative protocols for the preparation of functionalized benzenes.

Experimental Section

*Typical procedure for the preparation of 5-iodobiphenyl-3-carbaldehyde (**3a**)*

I_2 (1 mmol) was added to a flask containing 4-phenylhepta-1,2-dien-6-yn-4-ol (**2a**, 1 mmol) in CH_3CN (5 mL). The solution was stirred under reflux. Upon completion, the mixture was concentrated under vacuum. The residue was purified by column chromatography on silica gel using ethyl acetate/hexanes (1:20–1:5) as the eluent to give 5-iodobiphenyl-3-carbaldehyde (**3a**, 75 %). **3b**–**3x** were obtained in a similar manner.

*Typical procedure for the preparation of (5-iodobiphenyl-3-yl)(phenyl) methanone (**4a**)*

I_2 (0.5 mmol) was added to a flask containing 4,7-diphenylhepta-1,2-dien-6-yn-4-ol (**2z**, 0.5 mmol) in CH_3CN (5 mL). The solution was stirred under reflux. Upon completion, the mixture was concentrated under vacuum. The residue was purified by column chromatography on silica gel using ethyl acetate/hexanes (1:20–1:5) as the eluent to give (5-iodobiphenyl-3-yl)(phenyl)methanone (**4a**, 68 %). **4b**–**4l** were obtained in a similar manner.

*Typical procedure for the preparation of 3-methylbiphenyl (**6a**)*

H_2SO_4 (1 mmol) was added to a flask containing 4-phenyl-hepta-1,2,6-trien-4-ol (**5a**, 1 mmol) in CH_2Cl_2 (5 mL) was stirred at room temperature. Upon completion, the reaction was quenched with aqueous Na_2CO_3. The mixture was extracted with ethyl acetate (5 mL × 3). The combined organic phases were dried, filtered, and concentrated under vacuum. The residue was purified by column chromatography on silica gel using ethyl acetate/hexanes (1:80) as the eluent to give 3-methylbiphenyl (**6a**, 81 %). **6b**–**6t** were obtained in a similar manner.

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Keywords: allenes · domino reactions · iodoaryl ketones · iodobenzaldehydes · synthetic methods

[1] a) X. Y. Guo, C. J. Li, *Org. Lett.* **2011**, *13*, 4977–4979; b) Y. Y. Liu, J. P. Wan, *Org. Biomol. Chem.* **2011**, *9*, 6873–6894; c) R. Chinchilla, C. Nájera, *Chem. Soc. Rev.* **2011**, *40*, 5084–5121; d) C. L. Sun, Y. F. Gu, W. P. Huang, Z. J. Shi, *Chem. Commun.* **2011**, *47*, 9813–9815; e) M. Omote, M. Tanaka, A. Ikeda, S. Nomura, A. Tarui, K. Sato, A. Ando, *Org. Lett.* **2012**, *14*, 2286–2289.

[2] a) C. Y. Wu, Y. C. Lin, P. T. Chou, Y. Wang, Y. H. Liu, *Dalton Trans.* **2011**, *40*, 3748–3753; b) P. García-García, A. Martínez, A. M. Sanjuán, M. A. Fernández-Rodríguez, R. Sanz, *Org. Lett.* **2011**, *13*, 4970–4973; c) H. W. Zhou, Y. P. Xing, J. Z. Yao, J. H. Chen, *Org. Lett.* **2010**, *12*, 3674–3677; d) V. E. Ziffle, P. Cheng, D. L. J. Clive, *J. Org. Chem.* **2010**, *75*, 8024–8038; e) Y. X. Shen, H. F. Jiang, Z. W. Chen, *J. Org. Chem.* **2010**, *75*, 1321–1324.

[3] a) A. G. Myers, E. Y. Kuo, N. S. Finney, *J. Am. Chem. Soc.* **1989**, *111*, 8057–8059; b) A. G. Myers, P. S. Dragovich, E. Y. Kuo, *J. Am. Chem. Soc.* **1992**, *114*, 9369–9386; c) R. Nagata, H. Yamanaka, E. Okazaki, I. Saito, *Tetrahedron Lett.* **1989**, *30*, 4995–4998; d) R. Nagata, Y. Hidenori, E. Murahashi, I. Saito, *Tetrahedron Lett.* **1990**, *31*, 2907–2910; e) A. G. Myers, P. S. Dragovich, *J. Am. Chem. Soc.* **1989**, *111*, 9130–9132.

[4] a) S. M. Ma, *Chem. Rev.* **2005**, *105*, 2829–2871; b) S. Sakai, M. Nishitani, *J. Phys. Chem. A* **2010**, *114*, 11807–11813; c) K. Gilmore, I. V. Alabugin, *Chem. Rev.* **2011**, *111*, 6513–6556; d) M. Schmittel, A. A. Mahajan, G. Bucher, *J. Am. Chem. Soc.* **2005**, *127*, 5324–5325; e) J. Zhao, C. O. Hughes, F. D. Toste, *J. Am. Chem. Soc.* **2006**, *128*, 7436–7437.

[5] a) X. S. Fan, Y. Y. Wang, Y. Y. Qu, H. Y. Xu, Y. He, X. Y. Zhang, J. J. Wang, *J. Org. Chem.* **2011**, *76*, 982–985; b) X. Y. Zhang, X. F. Jia, L. L. Fang, N. Liu, J. J. Wang, X. S. Fan, *Org. Lett.* **2011**, *13*, 5024–5027; c) H. Y. Xu, X. Y. Zhang, Y. He, S. H. Guo, X. S. Fan, *Chem. Commun.* **2012**, *48*, 3121–3123.

[6] For a recent preparation and reaction of hydroxylated 1,5-allenynes, see: J. Ma, L. L. Peng, X. Zhang, Z. Zhang, M. Campbell, J. B. Wang, *Chem. Asian J.* **2010**, *5*, 2214–2220.
[7] a) L. P. Feng, D. Kumar, D. M. Birney, S. M. Kerwin, *Org. Lett.* **2004**, *6*, 2059–2062; b) H. Hibbert, *J. Am. Chem. Soc.* **1915**, *37*, 1748–1763; c) G. Stavber, M. Zupan, S. Stavber, *Tetrahedron Lett.* **2006**, *47*, 8463–8466.
[8] The molecular structure of **3 f** was determined by X-ray crystallographic analysis. CCDC 884851 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
[9] For I_2-promoted formation of carbocation from tertiary alcohol, see: J. Choi, G. H. Lee, I. Kim, *Synlett* **2008**, 1243–1249.
[10] For I_2-promoted cyclizations, see: a) L.-J. Wang, H.-T. Zhu, L. Lu, F. Yang, X.-Y. Liu, Y.-M. Liang, *Org. Lett.* **2012**, *14*, 1990–1993; b) F. Yang, K.-G. Ji, H.-T. Zhu, A. Shaukat, X.-Y. Liu, Y.-M. Liang, *Chem. Eur. J.* **2011**, *17*, 4986–4990; c) H.-T. Zhu, K.-G. Ji, F. Yang, L.-J. Wang, S.-C. Zhao, S. Ali, X.-Y. Liu, Y.-M. Liang, *Org. Lett.* **2011**, *13*, 684–687; d) B. Godoi, R. F. Schumacher, G. Zeni, *Chem. Rev.* **2011**, *111*, 2937–2980; e) B. Crone, S. F. Kirsch, K.-D. Umland, *Angew. Chem.* **2010**, *122*, 4765–4768; *Angew. Chem. Int. Ed.* **2010**, *49*, 4661–4664; f) A. Palisse, S. F. Kirsch, *Org. Biomol. Chem.* **2012**, *10*, 8041–8047; g) A. Sakakura, A. Ukai, K. Ishihara, *Nature* **2007**, *445*, 900–903; h) A. Sakakura, G. Shomi, A. Ukai, K. Ishihara, *Heterocycles* **2010**, *82*, 249–255; i) A. Sakakura, K. Ishihara, *Chim. Oggi* **2007**, *25*, 9–12.
[11] P. Neuhaus, *Synthesis and Characterization of Organic High-Spin Molecules*, doctoral dissertation, **2012**, Ruhr-Universität Bochum.
[12] a) J. N. Moorthy, N. Singhal, K. Senapati, *Tetrahedron Lett.* **2006**, *47*, 1757–1761; b) S. Das, A. K. Panigrahi, G. C. Maikap, *Tetrahedron Lett.* **2003**, *44*, 1375–1377; c) S. W. Kshirsagar, N. R. Patil, S. D. Samant, *Tetrahedron Lett.* **2008**, *49*, 1160–1162.
[13] The molecular structure of 3′-iodo-5′-(iodomethyl)biphenyl-4-carbonitrile (**V**) was determined by X-ray crystallographic analysis. CCDC 884853 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
[14] a) I. Nakamura, D. Zhang, M. Terada, *J. Am. Chem. Soc.* **2010**, *132*, 7884–7886; b) E. M. Cabaleiro-Lago, J. Rodriguez-Otero, R. M. Garcia-López, A. Pena-Gallego, J. M. Hermida-Ramon, *Chem. Eur. J.* **2005**, *11*, 5966–5974; c) C. S. López, O. N. Faza, F. P. Cossio, D. M. York, A. R. de Lera, *Chem. Eur. J.* **2005**, *11*, 1734–1738.
[15] H. Zhou, Y. Xing, J. Yao, Y. Lu, *J. Org. Chem.* **2011**, *76*, 4582–4590.
[16] a) B. Liu, R. S. Shetty, K. K. Moffett, M. J. Kelly, *Tetrahedron Lett.* **2011**, *52*, 1680–1684; b) J. Georgsson, C. Sköld, B. Plouffe, G. Lindeberg, M. Botros, M. Larhed, F. Nyberg, N. Gallo-Payet, A. Gogoll, A. Karlén, A. Hallberg, *J. Med. Chem.* **2005**, *48*, 6620–6631.

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