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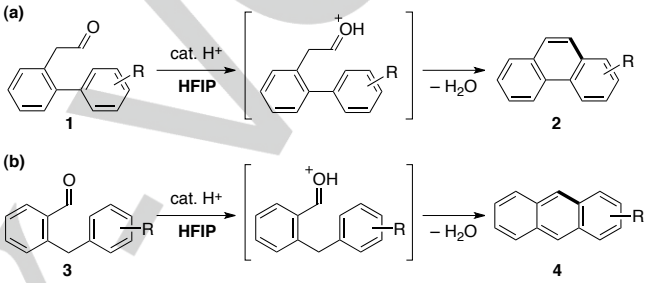
Facile Synthesis of Polycyclic Aromatic Hydrocarbons: Brønsted Acid-Catalyzed Dehydrative Cycloaromatization of Carbonyl Compounds in 1,1,1,3,3,3-Hexafluoropropan-2-ol

Takeshi Fujita, Ikko Takahashi, Masaki Hayashi, Jingchen Wang, Kohei Fuchibe, and Junji Ichikawa*

Abstract: Cycloaromatization of aromatic aldehydes and ketones was readily achieved by using a Brønsted acid catalyst in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP). In the presence of a catalytic amount of trifluoromethanesulfonic acid, (biaryl-2-yl)acetaldehydes and 2-benzylbenzaldehydes underwent sequential intramolecular cationic cyclization and dehydration to afford phenacenes and acenes, respectively. Furthermore, (biaryl-2-yl)acetaldehydes bearing a cyclopentene moiety at the α position underwent unprecedented cycloaromatization including ring expansion to afford triphenylenes. HFIP effectively promoted the cyclizations, suppressing side reactions presumably due to the stabilization of cationic intermediates.

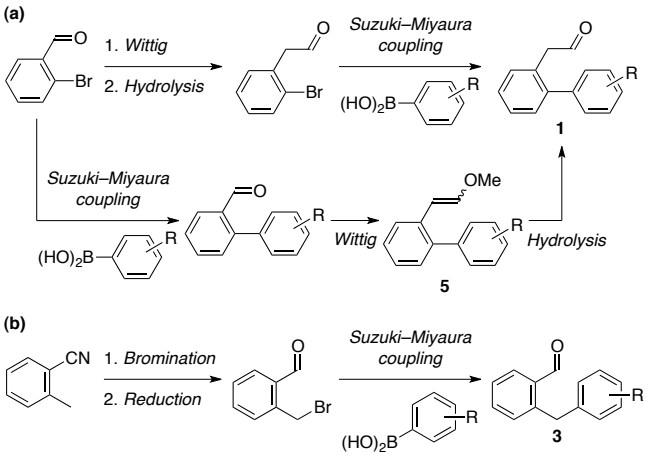
Polycyclic aromatic hydrocarbons (PAHs) are composed of fused aromatic rings, and their electronic properties, which are based on extended π-systems, have been intensively studied.[1] Among the PAHs, linear-shaped acenes and zigzag-shaped phenacenes have been especially found to have practical applications in electronic devices, such as organic field-effect transistors (OFETs).[2] Among conventional synthetic methods for acenes and phenacenes,[3–8] Brønsted acid-mediated dehydrative cycloaromatization of carbonyl compounds is one of the versatile approaches common to both acenes and phenacenes.[7,8] In this type of reaction, however, there is a drawback: an excess of acid is generally essential, although the entire reaction could in theory be mediated by a catalytic amount of acid. An excess of acid is used presumably because the desired reaction is otherwise sluggish. Particularly for phenacene synthesis, the presence of only a catalytic amount of acid increases the population of the more reactive enol forms via protonation and deprotonation, which might induce unwanted side reactions, such as aldol-type polymerizations.[9]

The solvent 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP) exhibits a substantial cation-stabilizing effect due to its high ionizing power with low nucleophilicity. Thus, we[10] and other groups[11,12] have utilized HFIP as a solvent in reactions involving cationic reagents and/or intermediates. We envisaged that HFIP would serve as an effective medium in the Brønsted acid-mediated cycloaromatization of carbonyl compounds to remove the drawback. Stabilizing the intermediary oxonium ions (protonated carbonyl compounds) should allow the use of a catalytic amount of acid. We herein demonstrate the Brønsted acid-catalyzed cycloaromatizations of (biaryl-2-yl)acetaldehydes **1** and 2-benzylbenzaldehydes **3** in HFIP, which readily provide phenacenes **2** and acenes **4**, respectively (Scheme 1).



Scheme 1. Brønsted acid-catalyzed synthesis of (a) phenacenes **2** from (biaryl-2-yl)acetaldehydes **1** and (b) acenes **4** from 2-benzylbenzaldehydes **3**.

The cyclization precursors, (biaryl-2-yl)acetaldehydes **1** and 2-benzylbenzaldehydes **3**, are both readily available as shown in Scheme 2. Aldehydes **1**, the precursors of phenacenes **2**, were prepared via the Suzuki–Miyaura cross-coupling of 2-(2-bromophenyl)acetaldehyde with arylboronic acids (Scheme 2a). Alternatively, aldehydes **1** were also prepared via Wittig/hydrolysis of 2-arylbenzaldehydes (Scheme 2a). Both intermediates were obtained from the same substrate, 2-bromobenzaldehyde via a Wittig/hydrolysis sequence and the Suzuki–Miyaura coupling, respectively (Scheme 2a). On the other hand, aldehydes **3**, the precursors of acenes **4**, were prepared via the Suzuki–Miyaura cross-coupling of 2-(bromomethyl)benzaldehyde, which were formed via a bromination/reduction sequence starting from 2-methylbenzonitrile, with arylboronic acids (Scheme 2b).[13]



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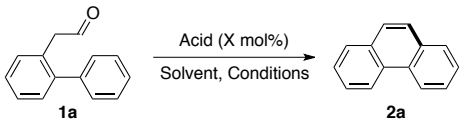
Scheme 2. Preparation of (a) (biaryl-2-yl)acetaldehydes **1** and (b) 2-benzylbenzaldehydes **3**.

To establish a versatile catalytic system, we sought suitable conditions for dehydrative cycloaromatization of (biphenyl-2-yl)acetaldehyde (**1a**) as a model substrate (Table 1). First, the solvent effect in the reaction of **1a** was examined in the presence of a stoichiometric amount of trifluoroacetic acid (Entries 1–5). While almost no cyclized products were obtained in toluene, dichloromethane, or acetonitrile (Entries 1–3), nitromethane afforded the cyclized product, phenanthrene **2a**, albeit in a low yield (Entry 4). Among the solvents examined, HFIP was found to be by far the most effective, affording a 92% yield of **2a** (Entry 5). When 10 mol% trifluoroacetic acid was used, the reaction was found to proceed catalytically (Entry 6). The choice of acid was also critical. Use of 10 mol% trifluoromethanesulfonic acid (TfOH), which is a stronger acid than trifluoroacetic acid, quantitatively afforded **2a** (Entry 7). Finally, only 4 mol% of TfOH in HFIP was sufficient to complete the reaction in 20 min at 0 °C, leading to a 93% yield of **2a** (Entry 8).

Table 1. Effects of solvents and acids on the dehydrative cycloaromatization of aldehyde **1a**.

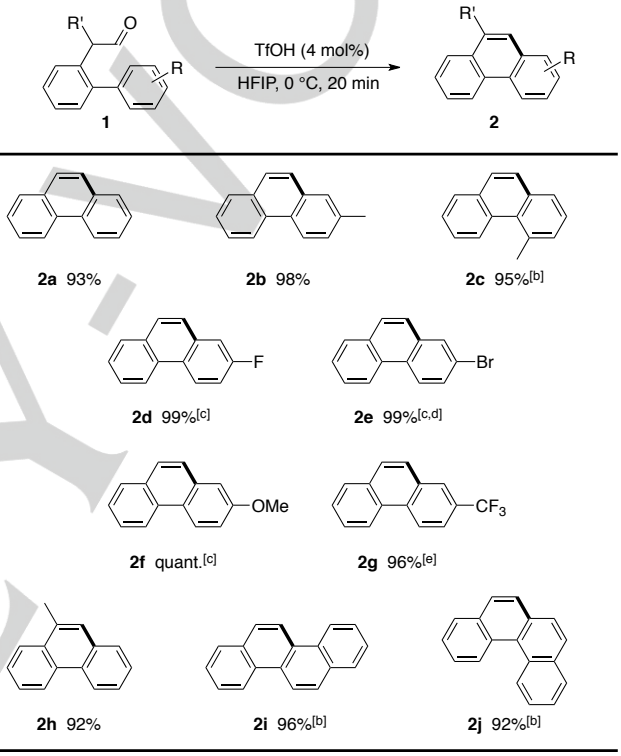


Entry	Acid	X [mol%]	Solvent	Conditions	Yield [%][a]
1	CF_3CO_2H	100	Toluene	RT, 16 h	1
2	CF_3CO_2H	100	CH_2Cl_2	RT, 16 h	1
3	CF_3CO_2H	100	CH_3CN	RT, 16 h	N.D.[b]
4	CF_3CO_2H	100	CH_3NO_2	RT, 16 h	13
5	CF_3CO_2H	100	HFIP	RT, 16 h	92
6	CF_3CO_2H	10	HFIP	RT, 16 h	41
7	TfOH	10	HFIP	0 °C, 20 min	98[c]
8	TfOH	4	HFIP	0 °C, 20 min	93[c]

[a] Yield was determined by ^{1}H NMR measurement using CH_2Br_2 as an internal standard. [b] N.D. = Not detected. [c] Isolated yield.

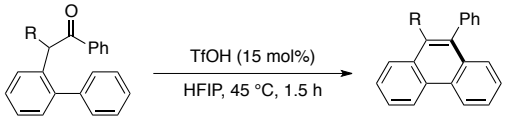
The optimal conditions obtained above for **1a** were then successfully applied to the cycloaromatization of other (biaryl-2-yl)acetaldehydes **1** with a variety of substituents on the nucleophilic aryl groups (Table 2). The reaction of *p*-tolyl- and *o*-tolyl-substituted phenylacetaldehydes **1b** and **1c** readily proceeded to afford 2-methylphenanthrene (**2b**) and 4-methylphenanthrene (**2c**), respectively, in excellent yields. Although the reactions of aldehydes **1d–g** bearing electron-deficient nucleophilic moieties were sluggish under the same conditions, higher catalyst loadings and/or longer reaction time dramatically improved the yields of the corresponding phenanthrenes **2d**–**g**. In particular, it is noted that aldehyde **1g** successfully underwent intramolecular cationic cyclization despite its reduced reactivity due to the strong electron-withdrawing CF_3 substituent on the nucleophilic benzene ring.[14] In addition, α-substituted aldehyde **1h** also participated in the cycloaromatization, affording 9-methylphenanthrene (**2h**) in a high yield. Aldehyde **1i** underwent regioselective cyclization on the α position of the 2-naphthyl group, leading to chrysene ([4]phenacene, **2i**) exclusively in 96% yield.[15] Cyclization on the β position of the 1-naphthyl group also proceeded effectively with substrate **1j** to produce [4]helicene (**2j**) in 92% yield.

Table 2. TfOH-catalyzed synthesis of substituted phenacenes **2** in HFIP.[a]



[a] Isolated yield. [b] TfOH (10 mol%). [c] TfOH (14 mol%). [d] 2 g scale. [e] TfOH (35 mol%), 80 min.

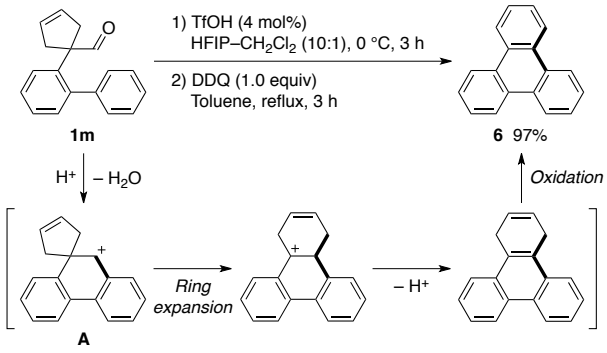
Furthermore, ketone substrates were employed in the TfOH-catalyzed dehydrative cyclization, despite steric hindrance around the carbonyl carbon (Eq. 1). Heating (biphenyl-2-yl)methyl phenyl ketone (**1k**) at 45 °C in the presence of 15 mol% TfOH afforded 9-phenylphenanthrene **2k** in 82% yield. Under the same conditions, α-substituted ketone **1l** gave 9,10-disubstituted phenanthrene **2l** in 58% yield.



(1)

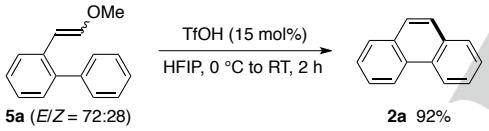
Intriguingly, the construction of two benzene rings was accomplished by conducting the abovementioned cyclization in combination with the ring expansion during the dehydration step. Thus, α,α-disubstituted (biphenyl-2-yl)acetaldehydes underwent

the acid-catalyzed cyclization followed by 1,2-migration of the α substituent.[16] In particular, aldehydes bearing a carbocyclic structure at the α position caused ring expansion as a result of 1,2-migration. Aldehyde **1m** bearing a cyclopentene moiety underwent the cyclization/ring expansion sequence followed by dehydrogenation with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) to afford triphenylene (**6**) in 97% yield (Eq. 2). In this reaction, the cationic intermediate **A** generated by dehydrative cyclization of **1m** underwent ring expansion to form a six-membered ring. This protocol can be a facile synthetic method for triphenylenes.[17]



(2)

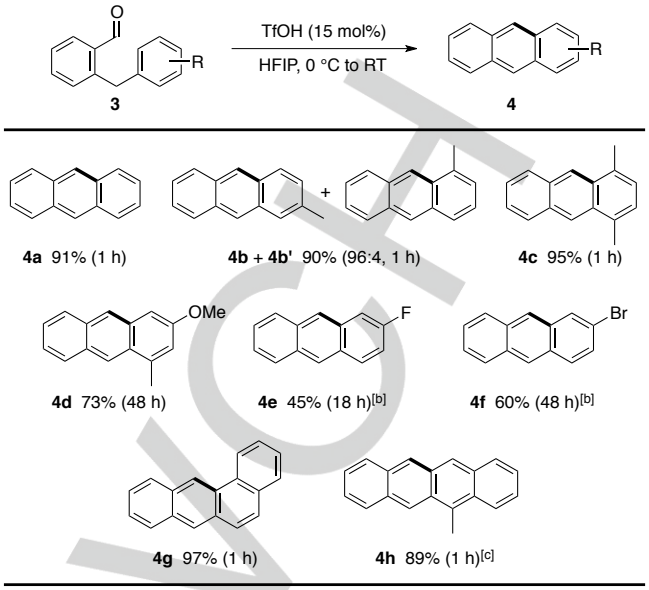
In addition, (biphenyl-2-yl)vinyl ether **5a**, hydrolysis of which led to **1a** (Scheme 2a), directly underwent a similar cyclization in the presence of the acid catalyst (Eq. 3).[18,19] On treatment with 15 mol% TfOH, cyclization of **5a** (*E*/Z = 72:28) proceeded via elimination of methanol to afford phenanthrene (**2a**) in 92% yield. Despite higher catalyst loading (15 mol%) and longer reaction time (2 h), cyclization of **5a** provided an effective approach to **2a**.



(3)

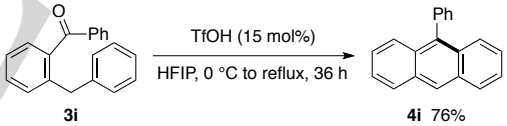
Next, the efficient synthesis of acenes **4** starting from 2-benzylbenzaldehydes **3** was examined via a similar dehydrative cycloaromatization (Table 3). On treatment of 2-benzylbenzaldehyde (**3a**) with 15 mol% TfOH, the expected anthracene (**4a**) was obtained in 91% yield. Cyclization of both electron-rich substrates **3b**–**d** and electron-deficient substrates **3e** and **3f** readily proceeded under the similar conditions to afford the corresponding anthracenes **4b**–**f** in good to high yields, although cyclization of halogen-bearing substrates **4e** and **4f** required heating. As with the cyclization of acetaldehyde **1i** (Table 2), cyclization of aldehyde **3g** proceeded exclusively at the α position of the 2-naphthyl group to afford tetraphene (**4g**).[15] In contrast, substrate **3h** bearing an 1-methyl-substituted naphthyl-2-yl group underwent cyclization on its β position, leading to the formation of 5-methyl-substituted tetracene **4h**.

Table 3. TfOH-catalyzed synthesis of substituted acenes **4** in HFIP.[a]

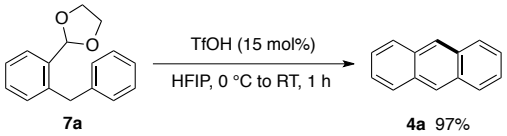


[a] Isolated yield. [b] Reflux. [c] Reaction was conducted in the dark.

2-Benzylbenzaldehyde analogues also participated in the cyclization. Synthesis of a 9-substituted anthracene was successfully achieved via the cyclization of a ketone substrate (Eq. 4). The TfOH-catalyzed cyclization of phenyl ketone **3i** proceeded to afford 9-phenylanthracene (**4i**) in 76% yield. Furthermore, an acetal derived from 2-benzylbenzaldehyde underwent a TfOH-catalyzed deacetalization/cycloaromatization sequence (Eq. 5).[20] Treatment of 2-(2-benzylphenyl)-1,3-dioxolane (**7a**) with a catalytic amount of TfOH afforded anthracene (**4a**) in 97% yield.



(4)



(5)

In summary, we have developed an efficient, atom-economical approach common to phenacenes, acenes, and triphenylenes via dehydrative cycloaromatization of aldehydes and ketones. In this process, only a catalytic amount of Brønsted acid was required for the formation of additional aromatic rings. The catalytic dehydrative cycloaromatization involving cationic cyclization was substantially promoted in HFIP. This methodology can be applied to the synthesis of a wide variety of PAHs, which may serve as next-generation electronic materials.

Experimental Section

Synthesis of 2-bromophenanthrene (**2e**): To an HFIP (72 mL) solution of (4'-bromobiphenyl-2-yl)acetaldehyde (**1e**, 1.97 g, 7.16 mmol) was added trifluoromethanesulfonic acid (90 μL, 1.0 mmol) at 0 °C. After stirring at

the same temperature for 20 min, the reaction was quenched with phosphate buffer (pH 7). Organic materials were extracted with CH_2Cl_2 three times, and the combined extracts were washed with brine and dried over Na_2SO_4. After removal of the solvents under reduced pressure, the residue was purified by silica gel column chromatography (hexane/CH_2Cl_2 = 5:1) to give 2-bromophenanthrene (**2e**, 1.83 g, 99%) as a white solid.

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Keywords: fluoroalcohols • Brønsted acids • catalysts • cyclization • aromatic compounds

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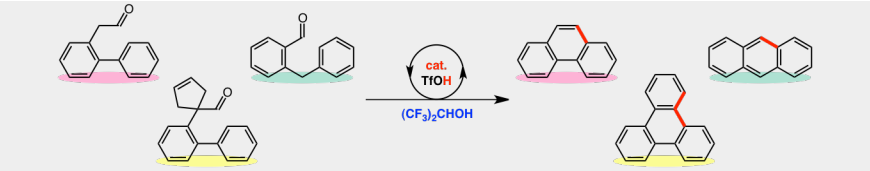
Key Topic: Cycloaromatization

COMMUNICATION



Cycloaromatization of aromatic aldehydes and ketones was readily achieved by using a Brønsted acid catalyst in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP). In the presence of a catalytic amount of trifluoromethanesulfonic acid, (biaryl-2-yl)acetaldehydes and 2-benzylbenzaldehydes underwent sequential intramolecular cationic cyclization and dehydration to afford polycyclic aromatic hydrocarbons (PAHs) including phenacenes, acenes, and triphenylenes. HFIP effectively promoted the cyclization, suppressing side reactions.

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Facile Synthesis of Polycyclic Aromatic Hydrocarbons: Brønsted Acid-Catalyzed Dehydrative Cycloaromatization of Carbonyl Compounds in 1,1,1,3,3,3-Hexafluoropropan-2-ol