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An unexpected thermal-ring-rearrangement of benzochromenes to inden-3-yl-naphthols with *p*TsOH†

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Described here is the first report of an unexpected thermal-ring rearrangement (TRR) of benzochromenes to indene derivatives promoted by *p*TsOH. This cascade ring-rearrangement proceeds through the protonation of benzochromenes by an acid catalyst followed by ring-opening and ring-closure by an intramolecular Friedel–Crafts cyclization to provide a new bicyclic framework, inden-3-yl-naphthols bearing a quaternary center, which also exhibited atropisomerism. Regioselectivity, broad substrate scope, high yields, solvent-free conditions and atom economy are the additional high points of this ring-rearrangement.

Introduction

Benzochromenes are versatile building blocks of natural products and part of many biologically significant molecules.[1] They are known to possess a spectrum of biological activities such as antifungal, anti-inflammatory, anti-hyperglycemic, cytotoxic and molluscicidal activities.[2] In addition to these features, benzochromenes are known to undergo a reversible ring-opening-cyclization process (Fig. 1) in a thermal/photochemical environment and hence exhibit photochromic properties,[3] and if this ring-opening-cyclization occurs in a specific acid–base medium, it leads to acidochromism.[3,4] As a result of photochromic and acidochromic properties, benzochromenes are known to possess significant material applications.[3–5]

Ring-rearrangement is conceptually different from the known ring-opening-cyclization reactions because at least two substrates are involved in the ring-opening-cyclization reactions,[6] whereas in ring-rearrangement reactions a single substrate is involved and rearranged to a new cyclic compound. Intramolecular ring-opening-cyclization reactions are also known as depicted in Fig. 1, but it is a reversible reaction (no rearrangement). To the best of our knowledge, these kinds of ring-rearrangements (RR) are not extensively investigated. However, there are some indirect examples, such as a cycloisomerization reaction, where the transformation of a polyunsaturated acyclic substrate initially cyclizes it to a less stable cyclic intermediate which further rearranges to a stable product.[7] Therefore in cycloisomerization reactions, the rearrangement of the less stable cyclic intermediate to a final (cyclic) product can be considered as a ring-rearrangement (RR) reaction. A couple of examples of RR are shown in Scheme 1, including our recent report on the cycloisomerization of 1,5-enyne, which proceeded through the formation of a less stable spirane, which then underwent a thermal-ring-rearrangement (TRR) with chloranil to yield the stable phenanthridinone (eqn (i), Scheme 1).[8] Another example is the cycloisomerization of bis(indolyl)methane tethered propargyl alcohol to yield a less stable spirane intermediate, which then underwent ring-rearrangement (RR) through 1,2-migration and yielded a stable carbazole (eqn (ii), Scheme 1).[9] With this background, herein we would like to report our first observation on the *p*TSA catalyzed thermal ring-rearrangement (TRR) of benzochromenes to inden-3yl-naphthols.

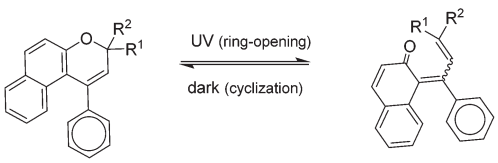

Fig. 1 Photochromism of benzochromenes (intramolecular-ring-opening-cyclization).

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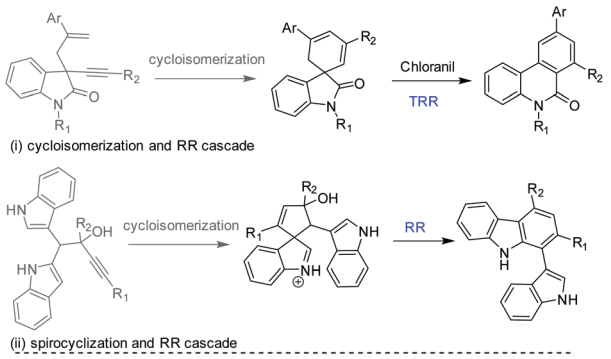
Results and discussion

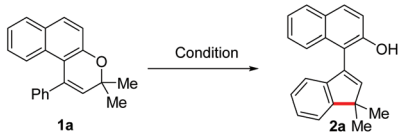
We commenced our investigations with 3,3-dimethyl-1-phenyl-3*H*-benzo[*f*]chromene (**1a**), which was synthesized using a



Scheme 1 Representative examples of ring-rearrangement (RR) reactions in cycloisomerizations.

known procedure.[10] Initially, **1a** was treated with the Lewis acid catalyst, $Ca(OTf)_2$ at 120 °C under solvent-free conditions for 48 h, unfortunately, we found that there was no change in the reaction; considering the solvent effect, the reaction was refluxed in toluene for 48 h, but no initiation of reaction was observed (entries 1 and 2, Table 1). Among the variety of Brønsted acids studied, TFA, CSA and benzoic acids (entries 4–6) were unable to catalyze the reaction, however to our delight PTSA gave 60% of product **2a** at 100 °C under solvent-free conditions after 16 h (entry 3).[11] The increase of temperature from 100 °C to 120 °C with 10 mol% PTSA was beneficial for elevating the yield of **2a** and also lessening the reaction time (entries 7 and 8). Interestingly, the maximum reaction yield (95%) was obtained with 20 mol% PTSA at 110 °C within 1.5 h (entry 9). It is worth mentioning that a further increase of catalyst loading and temperature did not have much influence on the reaction yield and time (entry 10). Among the various solvents screened (1,2-DCE, EtOH, CH_3CN, toluene, and water), it was found that the reaction yield of **2a** was best under solvent-free conditions (entries 11–15, Table 1).

Table 1 Optimization of the reaction conditions[a]



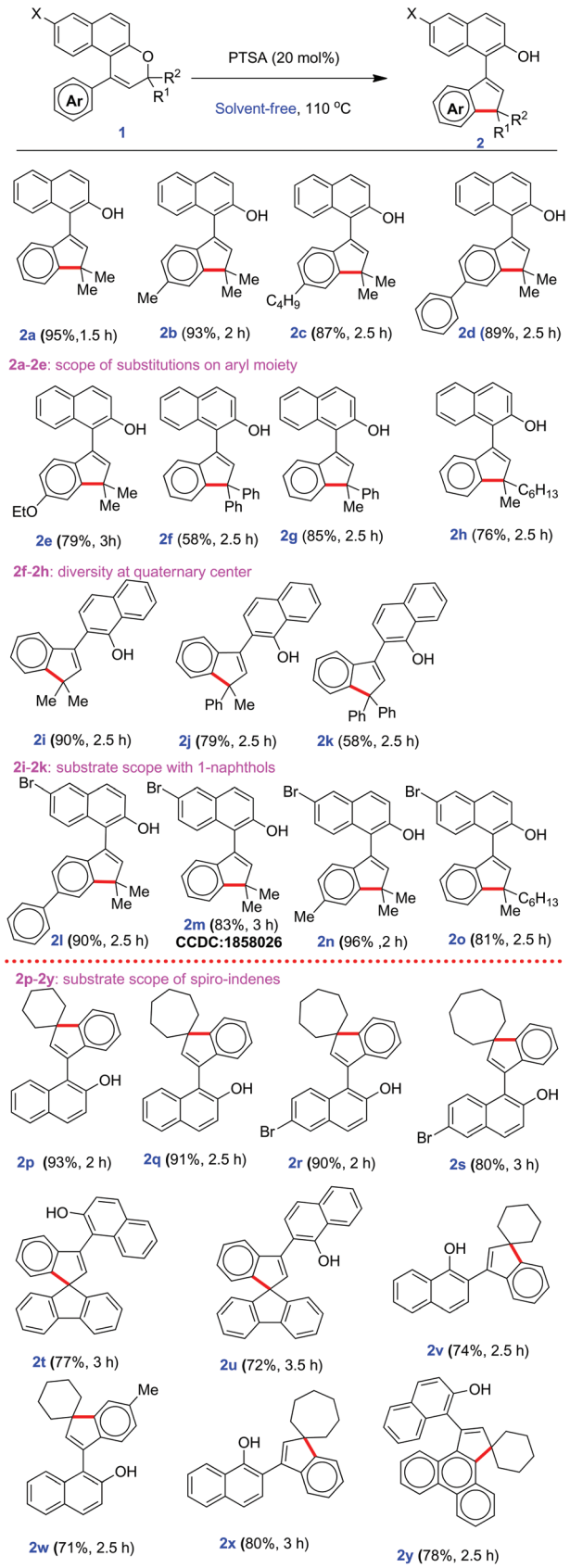
Entry	Catalyst (mol%)	Reaction conditions[a]	Yield[b] (%)
1	$Ca(OTf)_2/Bu_4NPF_6$, (10/10)	Neat, 120 °C, 48 h	nr
2	$Ca(OTf)_2/Bu_4NPF_6$, (10/10)	Toluene, 120 °C,48 h	nr
3	PTSA (10)	Neat, 100 °C, 16 h	60
4	TFA (100)	Neat, rt, 48 h	nr
5	CSA (20)	Neat, 110 °C, 48 h	nr
6	$PhCO_2H$ (30)	Neat, 110 °C, 48 h	nr
7	PTSA (10)	Neat, 110 °C, 6 h	91%
8	PTSA (10)	Neat, 120 °C, 4 h	92%
9	PTSA (20)	Neat, 110 °C, 1.5 h	95%
10	PTSA (40)	Neat, 120 °C, 1.5 h	78%
11	PTSA (20)	1,2-DCE, 90 °C, 14 h	20%
12	PTSA (20)	EtOH, 90 °C, 48 h	10%
13	PTSA (20)	CH_3CN, 90 °C, 48 h	nr
14	PTSA (20)	Toluene, 120 °C, 6 h	10%
15	PTSA (20)	H_2O, 100 °C, 48 h	nr

[a] Oil bath temperature. [b] Isolated yield; nr = no reaction, PTSA: *p*-toluene sulfonic acid, TFA: trifluoroacetic acid, CSA = 10-camphor sulfonic acid, OTf – trifluoromethane sulfonate.

Having discovered the optimum conditions for the ring-rearrangement of benzochromene (**1a**) to 1-(1,1-dimethyl-1*H*-inden-3-yl)naphthalen-2-ol (**2a**), we were keen to test the scope of different benzochromenes to rearrange into indene derivatives under the optimum conditions (Scheme 2). Therefore, we prepared several benzochromenes with different substitutions and subjected them to the standard reaction conditions (s.r.c). The ring rearrangement was compatible with alkyl (methyl, *n*-butyl), phenyl and ethoxy substitutions on the aryl ring to produce the corresponding-indene derivatives, **2b**, **2c**, **2d** and **2e** in excellent yields (Scheme 2). Substitutions at the quaternary center (phenyl–phenyl; phenyl–methyl; methyl–hexyl) of benzochromene (**1**) were retained during the TRR reaction to furnish indenes **2f–2h** in good yields. Interestingly, we observed that products **2g** and **2h** appeared as diastereomers in the ^1H and ^{13}C NMR spectra, which is due to the presence of a chiral carbon on the indene.[12] The crystal structure of the product (Fig. 2) shows that naphthyl and indenyl moieties are perpendicular to each other, and this may be analogous to a biphenyl system, so we presume that there could be a restricted rotation existing between the C–C single bond connecting naphthyl and indenyl moieties, which leads them to show atropisomerism. We may need to study this property more deeply to understand this phenomenon; however, our main objective here is to show the RR of benzochromenes.

In the case of TRR with 2-methyl-2,4-diphenyl-2*H*-benzo[*h*]chromene (**1j**) the product 2-(1-methyl-1-phenyl-1*H*-inden-3-yl)naphthalen-1-ol (**2j**) was yielded in 79% as a 1 : 1 mixture of diastereomers. In a similar way, other benzo[*h*]chromenes were also subjected to the standard TRR conditions and the 1-naphthol derivatives of indenes (**2i**, **2k**) were obtained in good yields. Bromonaphthol derivatives **2l–2o** were also formed from the corresponding benzochromenes through the TRR reaction in good to excellent yields. As expected, compound **2o** also exhibited atropisomerism due to the presence of a chiral carbon on the indene. The product 6-bromo-1-(1,1-dimethyl-1*H*-inden-3-yl)naphthalen-2-ol (**2m**) was found as a good crystalline solid, and hence the single crystal X-ray data of **2m** were obtained to confirm its structure (Fig. 2).[13] Furthermore, we examined the TRR of benzochromenes bearing the spiro-centre such as 1-phenylspiro[benzo[*f*]chromene-3,1′-cyclohexane] **1p** under standard reaction conditions and obtained the corresponding 1-(spiro[cyclohexane-1,1′-inden]-3′-yl)naphthalen-2-ol **2p** in 93% yield after 3 h (Scheme 2). Encouraged by this result, we prepared indene derivatives bearing cyclohexane (**2p**, **2v**, **2w**, **2y**), cycloheptane (**2q**, **2r**, **2x**), cyclooctane (**2s**) and fluorenyl (**2t**, **2u**) substitutions at the C1-spiro center in excellent yields from the corresponding spirocyclic-benzochromenes.

As depicted in Scheme 3, the synthesis of benzochromene (**1**) is known to begin from propargyl alcohol **3** and naphthol **4**



Scheme 2 Substrate scope of TRR reaction.

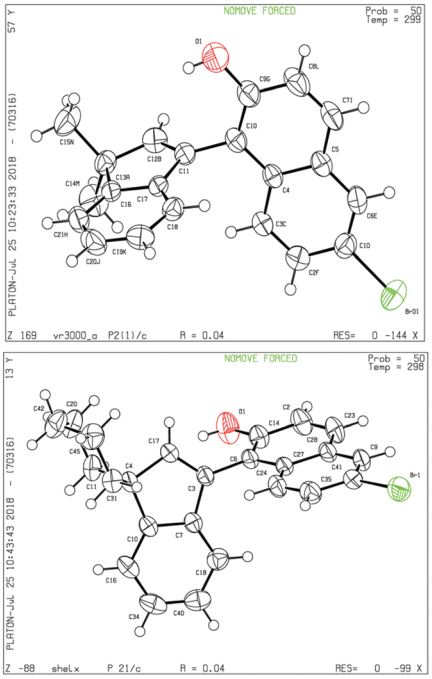
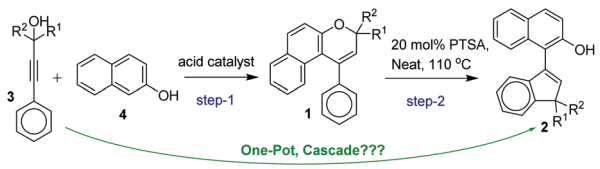


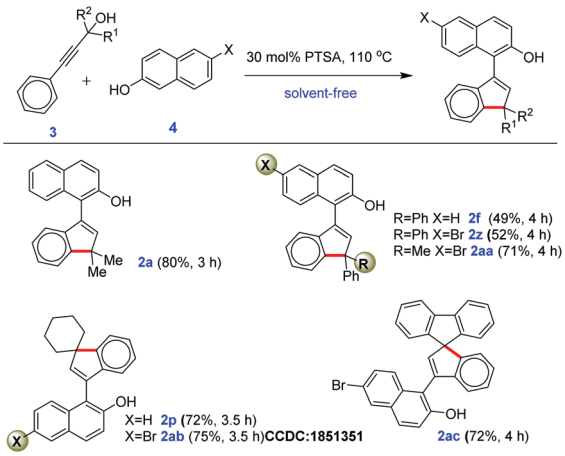
Fig. 2 ORTEP diagram of **2m** (top) and **2ab** (bottom) with 50% probability.



Scheme 3 The rationale for the one-pot cascade protocol.

using acid catalysts (step-1),[10] and here we discovered the TRR of benzochromene (**1**) to indene (**2**) in the presence of an acid catalyst (step-2, Scheme 3). Therefore, presuming that it is possible to develop a one-pot cascade reaction,[14] in such a way that **3** and **4** will form benzochromene **1** with PTSA, and then ring-rearrangement of **1** should give indene derivative **2** (Scheme 3).

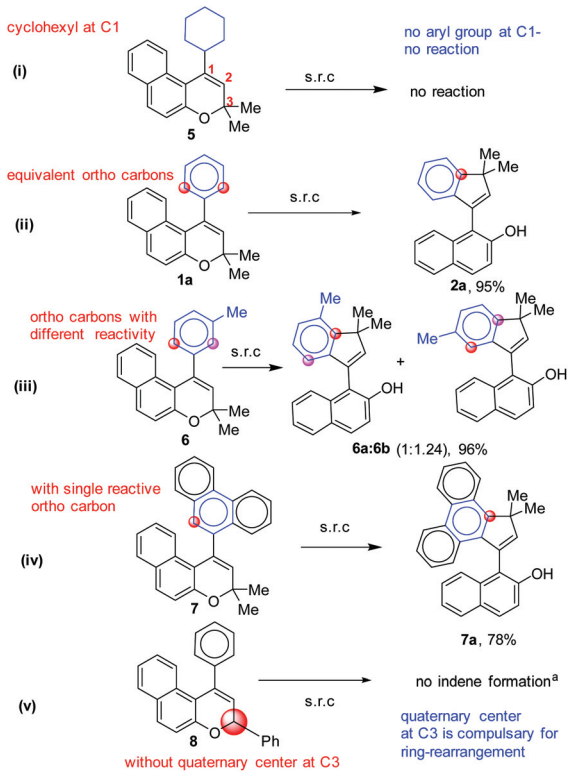
To implement this one-pot proposal, a mixture of 2-methyl-4-phenylbut-3-yn-2-ol (**3a**), 2-naphthol and PTSA was heated at 110 °C under solvent-free conditions and the formation of 3,3-dimethyl-1-phenyl-3*H*-benzo[*f*]chromene (**1a**) was observed in 20 min, and delightfully, further continuation of the reaction yielded the indene **2a** in 80% through the ring-rearrangement reaction (Scheme 4). Knowing the importance of a one-pot, cascade protocol towards a sustainable synthetic process,[14] we were encouraged to elaborate this method to synthesize some of the inden-3-yl-naphthols with diversity at the quaternary center (**2f**, **2z** and **2aa**) and with the spirocyclic system (**2p**, **2ab** and **2ac**) in a good overall yield. The structure of **2ab** was further confirmed by using single crystal X-ray data (Fig. 2).[13]



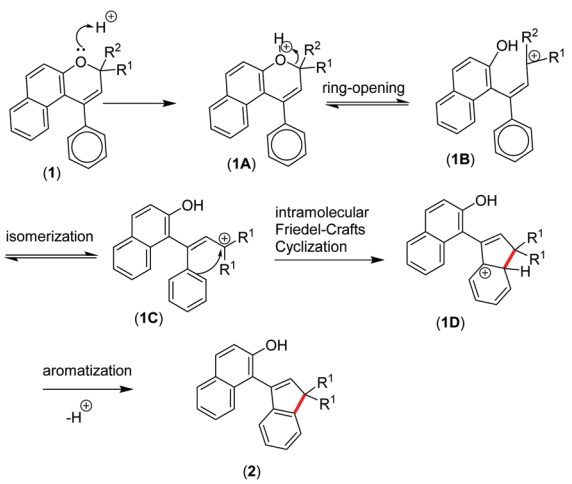
Scheme 4 One-pot synthesis. A mixture of 3 (1 equiv.), 4 (1.2 equiv.) and PTSA (30 mol%) was heated at 110 °C (oil bath temperature) for a specified time.

After developing a new TRR reaction of benzochromenes (Scheme 2) to indene derivatives and the one-pot reaction from propargyl alcohols (Scheme 4), we were interested in checking the scope and limitations of this method by performing control experiments as depicted in Scheme 5. The first reaction was performed with benzochromene **5** bearing a cyclohexyl moiety at C1 under standard reaction conditions (s.r.c.) and found that no change in the starting material was observed. This result emphasizes the importance of having an aryl group at C1 to accomplish the TRR reaction (eqn (i), Scheme 5). The second experiment was performed with benzochromene **1a** bearing a phenyl group at C1 with chemically equivalent *ortho*-carbons and accomplished the TRR (eqn (ii), Scheme 5). The third reaction was performed with a benzochromene (**6**) bearing a *meta*-tolyl group (with chemically inequivalent *ortho*-carbons) and a regioisomeric mixture of two indene derivatives (**6a**/**6b**) was obtained in a 1 : 1.24 ratio with 96% combined yield (eqn (iii), Scheme 5).[15] The fourth experiment commenced with the benzochromene **7** bearing a phenanthrenyl group at C1, with a single reactive *ortho*-carbon and accomplished the TRR to yield indene derivative **7a** in 78% yield (eqn (iv), Scheme 5). All these experiments (i–iv) concluded that it is must to have an aryl (phenyl) group at C1 with at least one reactive *ortho*-carbon to accomplish the TRR reaction. Later, we performed another reaction to check the importance of a quaternary center at C3 in TRR. Therefore we chose 1,3-diphenyl-3*H*-benzo[*f*]chromene (**8**), having a phenyl group with a reactive *ortho* carbon at C1 but not a quaternary center at C3 and subjected it to s.r.c., surprisingly, we found that the reaction did not yield the desired product (eqn (v), Scheme 5).[16] This experimental observation as a whole suggests that the TRR works with benzochromenes bearing a C3-quaternary center and aryl group at C1 with at least one reactive *ortho*-carbon.

Based on the observations made through the control experiments the plausible reaction mechanism for the PTSA catalyzed, thermal-ring-rearrangement (TRR) of benzochromene (**1**) to inden-3-yl-naphthol (**2**) is proposed in Scheme 6. Here, the Brønsted acid protonates the benzochromene **1** to form the oxonium **1A**, which then undergoes the ring-opening to yield carbocation intermediate **1B**. Isomerization of **1B** to **1C** followed by an intramolecular Friedel–Crafts cyclization and aromatization cascade provides the indene **2** with a ring rearrangement.



Scheme 5 Control experiments.



Scheme 6 The reaction mechanism for the TRR of benzochromenes.

Conclusions

In conclusion, we disclose here the first report on PTSA catalyzed, intramolecular thermal-ring-rearrangement (TRR) of benzochromenes to indene derivatives. Based on control experiments we confirmed that the presence of an aryl group with at least one reactive *ortho*-carbon at C1 and a quaternary center at C3 is must for the TRR of benzochromenes. We observed that these compounds exhibit atropisomerism, and in the case of **2g**, **2h**, **2j**, **2o**, and **2aa** we have noticed the formation of diastereomers in the ^{1}H and ^{13}C NMR spectra. Taking advantage of the benzochromene synthesis, from propargyl alcohols and naphthols, we developed further a green synthetic protocol by combining the benzochromene synthesis and their TRR in a one-pot, cascade strategy under solvent-free conditions. Further investigations towards the TRR concepts are in progress.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references

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11 Refer to the ESI† for the confirmation of the product.

12 ^{1}H and ^{13}C NMR spectra suggested that the rotamers are almost in a 1 : 1 ratio (see the ESI†).

13 Refer to the ESI† for the details of the single crystal X-ray data.

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15 The ratio of the regioisomeric mixture is calculated based on the ^{1}H NMR spectrum.

16 Benzochromene **8** was consumed and gave a complex mixture but not the desired indene derivative.