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Access to Naphthoic Acid Derivatives through an Oxabenzonorbornadiene Rearrangement

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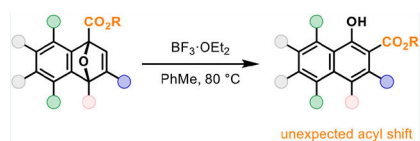Present Address: Honeywell Specialty Chemicals Seelze GmbH, Seelze 30926, Germany

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Abstract

Herein, the synthesis of 1-hydroxy-2-naphthoic acid esters through an unexpected Lewis-acid-mediated 1,2-acyl shift of oxabenzonorbornadienes is reported. Using this methodology, novel substitution patterns for 1-hydroxy-2-naphtoic acid esters can be obtained. A mechanistic proposal and rationale for this transformation, the products of which had been previously incorrectly characterized, is given.

Graphical Abstract

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Supporting Information

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Experimental procedures and analytical data for all oxabenzonorbornadienes and naphthoic acid ester derivatives (PDF)

During the course of a natural product synthesis project, we observed an unexpected Lewis-acid-catalyzed acyl shift of an oxabenzonorbornadiene, leading to the formation of a 1-hydroxy-2-naphthoic acid ester (Scheme 1A). While alkyl shifts of 1,4-disubstituted oxabenzonorbornadienes had been observed previously—primarily as undesired side reactions (Scheme 1B) in the presence of Lewis acids[1]—the cation-induced migration of electron-deficient acyl groups is some-what rare. Notably, the observed acyl shift (Scheme 1A) occurred in the absence of a substituent at C4 (see **1** for numbering), whereas all of the previously reported alkyl shifts are in the presence of a C4 substituent, indicating differing reactivity with an ester substituent at C1. In addition, as outlined in Scheme 1C, a supposed shift of the bridging oxygen atom of oxabenzonorbornadiene **5** was reported previously by using various metal complexes to facilitate the process.[2] However, comparison of the reported analytical data for **6**[2] with our own and analysis of data for **6**[3] and **7**[4] (see Table 1 and Figure 1) from the literature revealed that the conversion of **5** → **6** was a misassignment and, in fact, an acyl shift had occurred in that case as well. On the basis of these findings and our observation that esters can migrate similarly to alkyl substituents (at least from C1) in oxabenzonorbornadienes, we decided to investigate these rearrangements in more detail with the aim of gaining a better understanding of the scope and limitations of these transformations. Herein, we report a general entry to 1-hydroxy-2-naphthoic acid derivatives, which are versatile synthetic intermediates. Our approach is complementary to existing methods in that it provides access to differently substituted naphthoic acid derivatives that have previously been challenging to prepare.[5]

We initiated our optimization of the reaction conditions for the formation of naphthoic acid derivative 7 (selected examples are shown in Table 1; for more details see the Supporting Information) using different Lewis acids known to facilitate alkyl shifts in the corresponding alkyl-substituted oxabenzonorbornadiene substrates (see entries 1–5).[1a–c] 1,2-Dichloroethane was used as solvent in line with previously described alkyl shifts.[1a,d] Boron trifluoride diethyl etherate emerged as the most efficient Lewis acid to facilitate the acyl shift at room temperature. However, at elevated temperature (entry 6) a significant drop in yield was observed due to nonspecific decomposition. In contrast, reduced decomposition was observed when the solvent was changed to toluene. At room temperature, a slight drop in yield was observed (entry 7); however, the yield increased upon raising the reaction temperature to 80 °C (entry 8). When substoichiometric amounts of Lewis acid were used (entry 9), the starting material was not fully consumed. Finally, an optimal yield was obtained upon shortening the reaction time to 2 h (entry 10).

With the optimized conditions in hand, substrates bearing different substituents on the A-ring were investigated in the transformation (Figure 1). For substrates bearing substitution at C4, good to excellent yields were obtained (see **8–12**). The synthesis of 1-hydroxy-2-naphthoic acid esters bearing a *para*-nitro-arene (**10**) or a halogen (**12**) are especially noteworthy, since products bearing these functionalities have proven challenging to access through existing methodologies. (e.g., refs 5a, 5f, and 5g). Substituents at C3 were also tolerated, leading to fully substituted A-rings (see **13–15**). In these compounds, the presence of different halogen atoms allows for potential further functionalization through cross-coupling. Acyl migration was disfavored for oxabenzonorbornadienes with substituents at

C3. In these cases, 4-hydroxy-1-naphthoic acid esters were obtained as the major products (**16** and **17/18**). Substitution at C2 was accommodated, and the acyl shift occurred to afford β-keto ester **19** bearing a quaternary carbon atom in the α-position. In addition to investigating the effect of different substituents on the oxabenzonorbornadiene substrates, the migration potential of different esters was investigated as well (**20–23**). The yields obtained for an ethyl, the bulkier *iso*-propyl, and an allyl ester were comparable to those obtained for the methyl ester. On the other hand, a significant drop in yield was observed for the formation of benzyl ester **23,** and the analogous *tert*-butyl ester **24** was not formed under the reaction conditions, likely undergoing facile hydrolysis followed by nonproductive decomposition.

With regard to substituents on the B-ring (Figure 2), symmetrical substitution patterns were investigated first, affording the corresponding 1-hydroxy-2-naphthoic acid esters in good yield (**25–28**). Electron-donating and electron-withdrawing groups were well tolerated. However, for substrates bearing a single substituent at either C5 or C8, different electronic directing effects were observed. For example, with an electron-donating methoxy substituent at C5, acyl migration occurs to give 1-hydroxy-2-naphthoic acid ester **29** as the sole product. In contrast, a substrate bearing a methoxy substituent at C8 favored the formation of 1-hydroxy-4-naphthoic acid ester **30,** which was obtained along with 1-hydroxy-2-naphthoic acid ester **31.** To further ascertain the directing influence of groups on the arene portion of the oxabenzonorbornadienes, substrates bearing a methyl group at C3 and a methoxy group at either C5 or C8 were synthesized. In the case of the substrate bearing 3,8-substitution, 1-hydroxy-4-naphthoic acid ester **32** was formed exclusively, presumably due to the matched electronic directing effects of both substituents. For the substrate bearing 3,5-substitution, 1-hydroxy-2-naphthoic acid ester **33** was obtained as the only isolable product—in line with the stronger directing influence of a methoxy group over a methyl group. A substrate possessing an extended aromatic ring also participated in the acyl shift transformation to give anthracene **34.** However, the yield dropped significantly in comparison to that of the reaction of the oxabenzonorbornadienes.

On the basis of our observations, we propose the following mechanisms for selective formation of the different observed products for substrates bearing different substituents. We believe the oxa-bridge opening to be the product-determining step, wherein selectivity is dictated by the relative stability of the carbocationic intermediates that can be formed by heterolytic cleavage of either bridging C–O bond. For the formation of 1-hydroxy-2-naphthoic acid esters, we propose opening of the oxa-bridge occurs to form an allylic and benzylic carbocation at C4 (Scheme 2, A). The preference for ionization at C4 likely arises because of the destabilizing inductively electron-withdrawing effect of the ester group on an incipient carbocation at C1. The observed oxa-bridge opening selectivity holds even when R = H (see 7) where the formation of a secondary carbocation is favored. From carbocation **A**, a 1,2-acyl shift occurs, followed by rearomatization through the loss of a proton. The proposed acyl-shift is in accordance with previously observed 1,2-acyl shifts in (Lewis) acid mediated rearrangements.[6–9] Cleavage of the O–B bond upon hydrolytic workup leads to the 1-hydroxy-2-naphthoic acid ester products. The stoichiometric formation of an O–B bond

is supported by the observation that using substoichiometric amounts of Lewis acid in the reaction only afforded partial conversion.

For the formation of the 1,4-substituted products (e.g., **16** and **17**), we propose that the reaction proceeds through intermediate **D**, bearing a carbocation at C1 (scheme 3).The switch in regioselectivity of the oxa-bridge opening can be rationalized by the presence of a substituent at C3 stabilizing resonance structures **D** and **E** by rendering the carbocation tertiary and allylic as well as additional stability due to the extended π-system. In addition, the lack of a substituent at C4 reduces the likelihood of of oxa-bridge opening at C4. Rearomatization from **D** or **E** likely occurs through a 1,2-hydride shift, followed by the loss of a proton. Evidence for a hydride shift during the formation of naphthols from oxabenzonorbornadienes was first reported by Vernon and co-workers.[10] Alternatively, a simple deprotonation would yield the boron enolate, which will give the naphthol following protonation. Subsequent hydrolysis would lead to 1-hydroxy-4-naphthoic ester.

In summary, we report a novel approach to 1-hydroxy-2-naphthoic acid esters through an unexpected acyl shift. Using this approach, novel substitution patterns can be accessed. In certain cases, the formation of 1-hydroxy-4-naphthoic acid esters was observed instead of the expected formation of 1-hydroxy-2-naphthoic acid esters. The formation of the different constitutional isomers can be rationalized by the electronic properties of the different directing substituents. This work also served to correct a previously reported misassignment of the products of the rearrangement of related oxabenzonorbornadienes.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

ACKNOWLEDGMENTS

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

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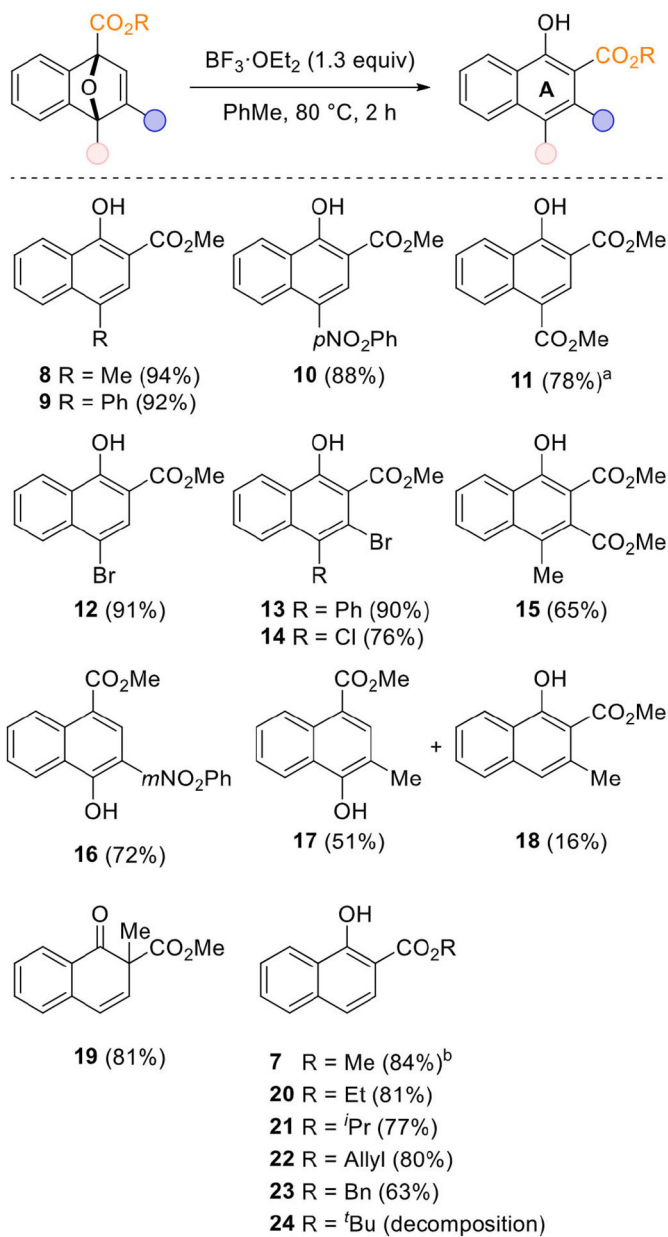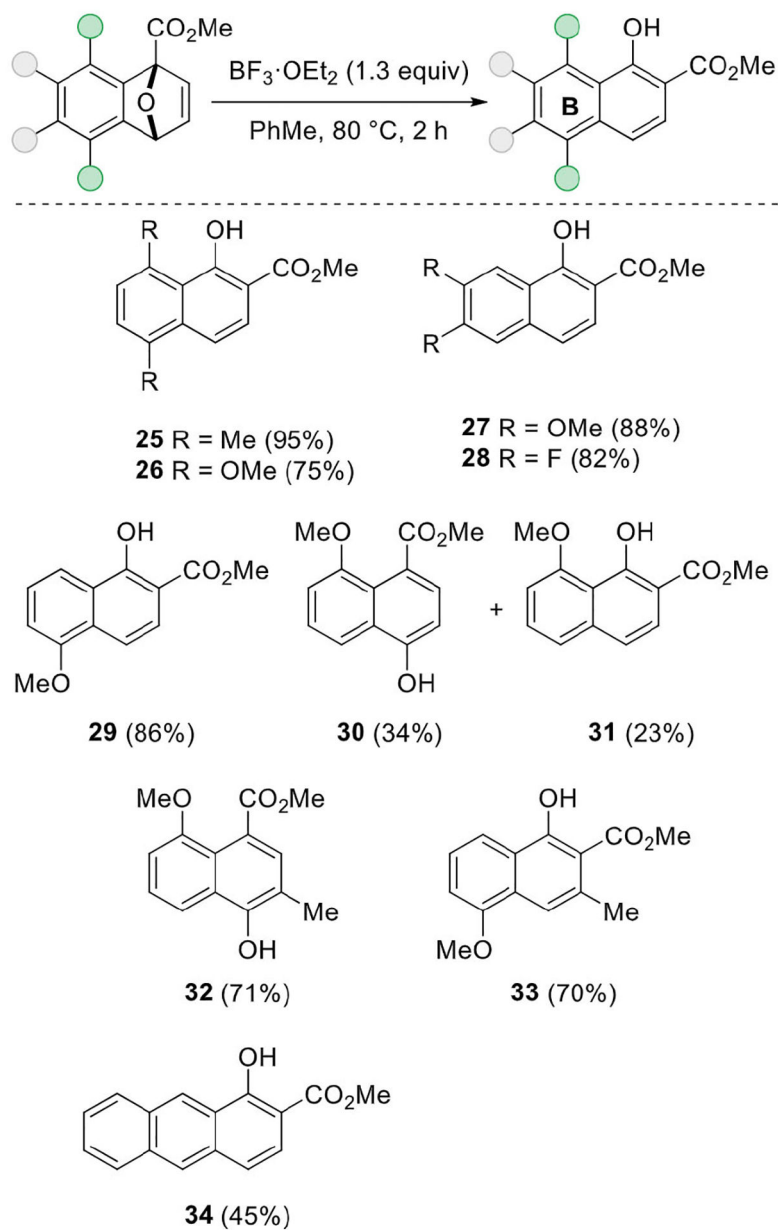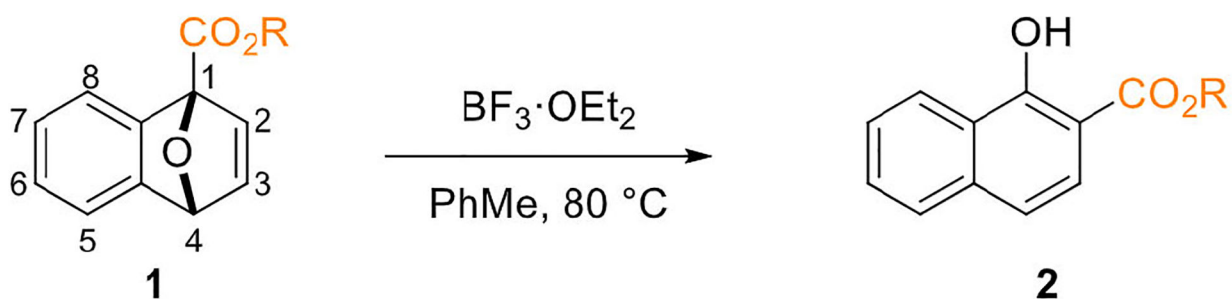
Figure 1.

Scope of the A-ring substituents. Reactions were performed on a 0.20 mmol scale. [a]2.0 equiv of BF₃·OEt₂ was used. [b]The reaction was performed on a 1.00 mmol scale, providing 170 mg (0.84 mmol) of 7.

Figure 2.
Scope of the B-ring substituents. Reactions were performed on a 0.20 mmol scale.
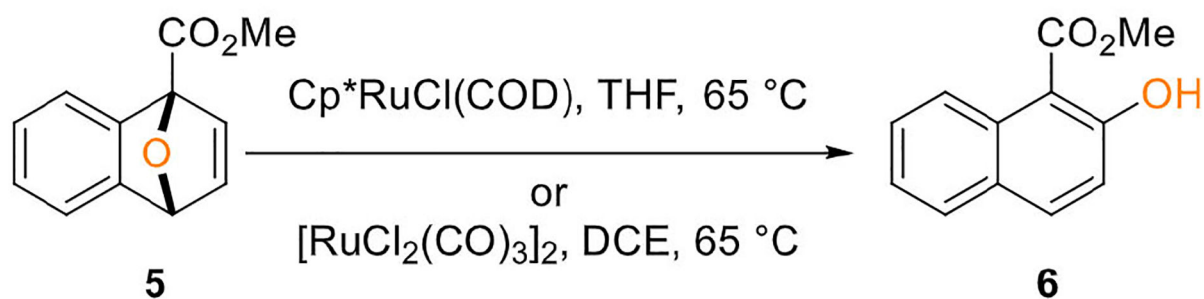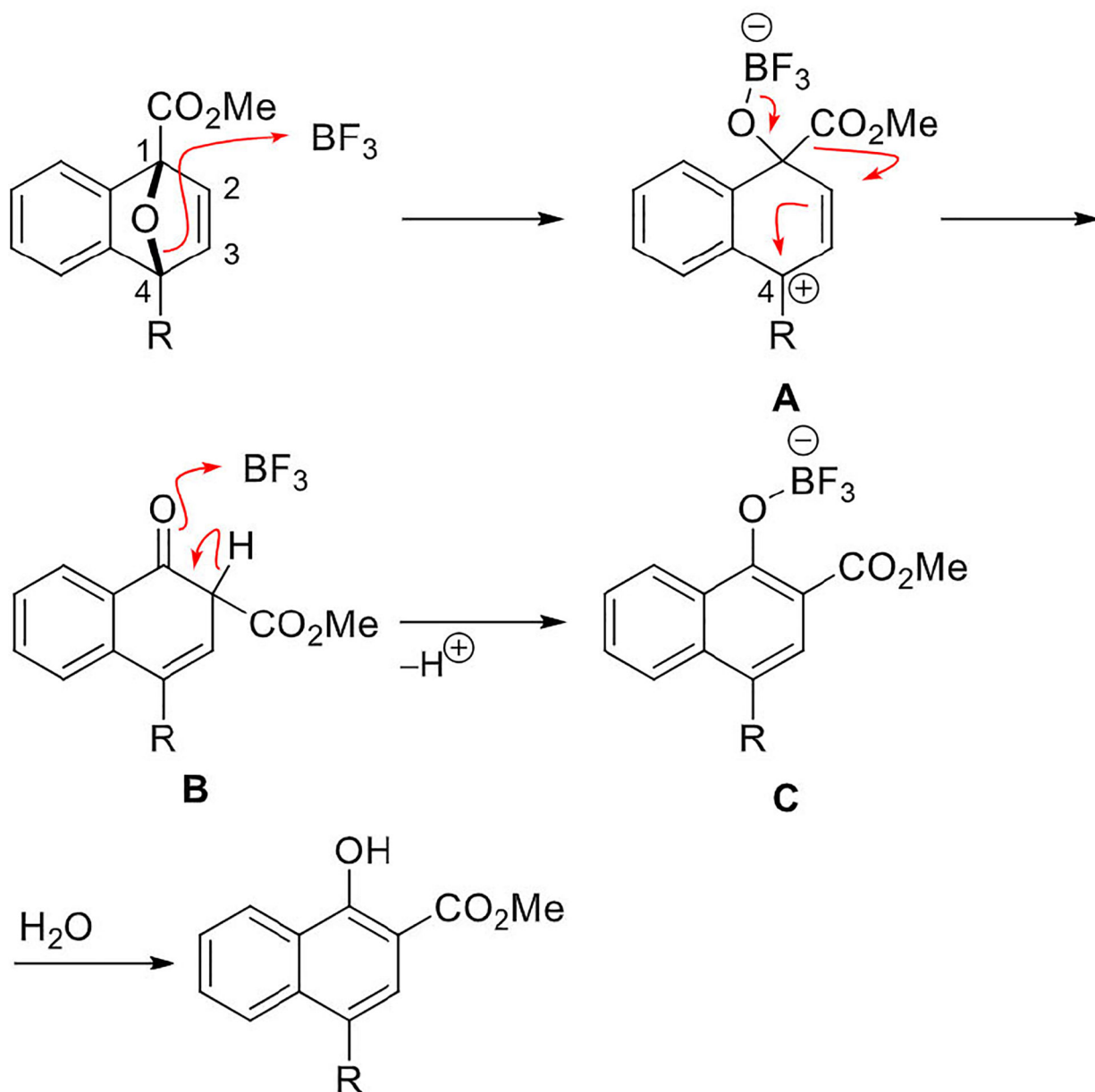
A: this work

B: previously described 1,2-alkyl shifts of oxabenzonorbornadienes
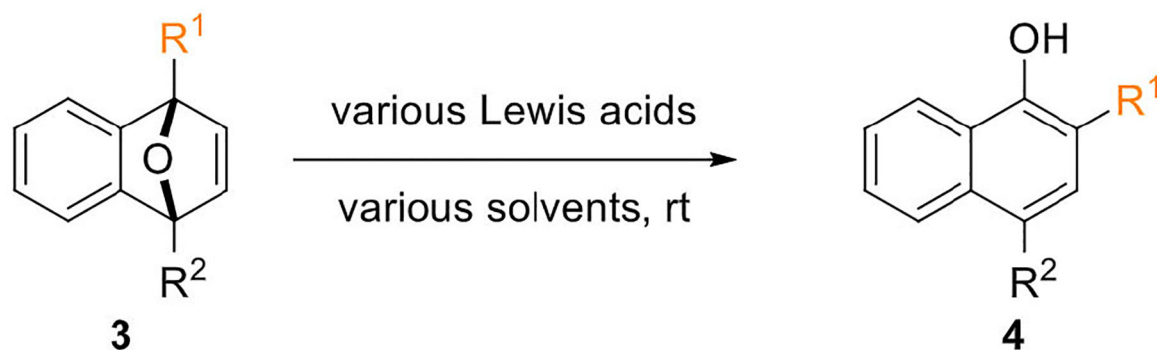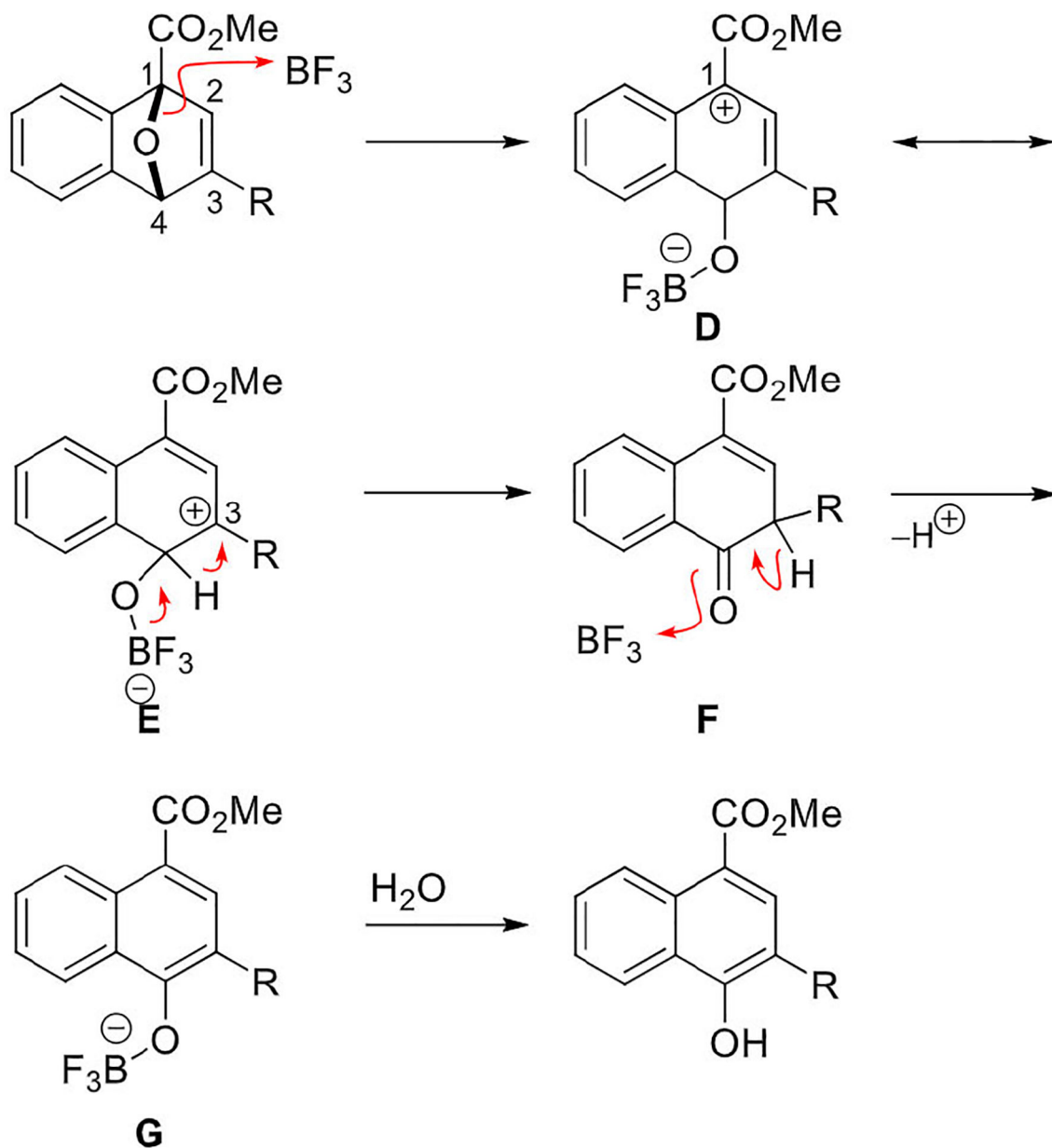

C: previously described 1,2-O shift (misassigned)

Scheme 1.
Rearrangements of Oxabenzonorbornadienes

Scheme 2.
Proposed Mechanism for the Formation of 1-Hydroxy-2-naphthoic Acid Esters

Scheme 3.
Proposed Mechanism for the Formation of 1-Hydroxy-4-naphthoic Acid Esters

Table 1.

Selected Results of the Optimization for the Rearrangement of Oxabenzonorbornadiene 5
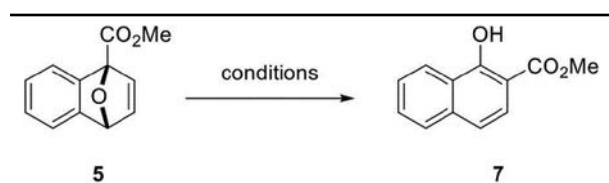
entry	Conditions[a]	Yield[b]
1	InCl$_3$, DCE, rt, 14 h	59%
2	In(OTf)$_3$, DCE, rt, 14 h	traces
3	Cu(OTf)$_2$, DCE, rt, 14 h	68%
4	Sc(OTf)$_3$, DCE, rt, 14 h	51%
5	BF$_3$.OEt$_2$, DCE, rt, 14 h	75%
6	BF$_3$.OEt$_2$, DCE, 60 °C, 14 h	59%
7	BF$_3$.OEt$_2$, PhMe, rt, 14 h	70%
8	BF$_3$.OEt$_2$, PhMe, 80 °C, 14 h	87%
9	BF$_3$.OEt$_2$,[c] PhMe, 80 °C, 14 h	47%
10	BF$_3$.OEt$_2$, PhMe, 80 °C, 2 h	91% (84%)[d]

[a]All reactions were run with IO mg (0.05 mmol) of **5** and 1.3 equiv of Lewis acid.

[b]Isolated yield after purification by preparative TLC.

[c]0.5 equiv of Lewis acid was used.

[d]The reaction was conducted on a l.OO mmol scale and purified by column chromatography, providing 170 mg (0.84 mmol) of **7**.