A Journal of the Gesellschaft Deutscher Chemiker

Angewandte International Edition GDCh Chemie

www.angewandte.org

Accepted Article

Title: Unusual Skeletal Reorganization of Oxetanes for the Synthesis of 1,2-Dihydroquinolines

Authors: Guannan Wang, Hai Huang, Wengang Guo, Chenxiao Qian, and Jianwei Sun

To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.201916727
Angew. Chem. 10.1002/ange.201916727

Link to VoR: http://dx.doi.org/10.1002/anie.201916727
http://dx.doi.org/10.1002/ange.201916727

WILEY-VCH

10.1002/anie.201916727

WILEY-VCH

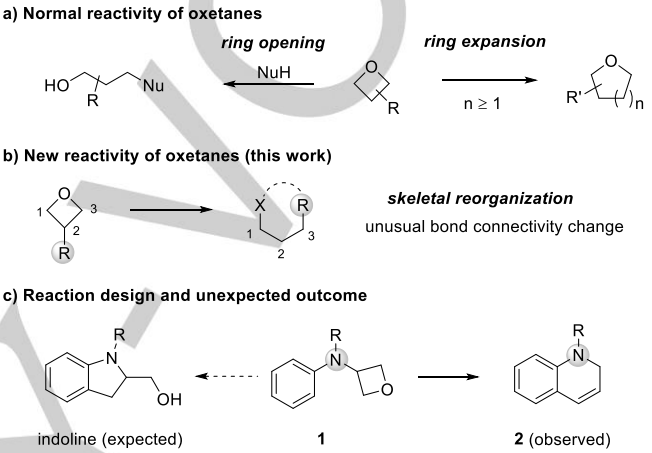
Unusual Skeletal Reorganization of Oxetanes for the Synthesis of 1,2-Dihydroquinolines

Guannan Wang,[+] Hai Huang,[+] Wengang Guo, Chenxiao Qian, and Jianwei Sun*

***Abstract**: Skeletal reorganization is a type of fascinating transformations owing to their intriguing mechanisms and utility in complex molecule synthesis. However, these reactions are limitedly known for most functional groups. Herein, we describe such an unusual process of oxetanes. In the presence of In(OTf)$_3$ as catalyst, oxetane-tethered anilines reacted unexpectedly to form 1,2-dihydroquinolines. This process not only provides expedient access to dihydroquinolines, but also represents a new reaction of oxetane. Mechanistically, it is believed that the reaction proceeds via initial nitrogen attack rather than arene attack followed by a series of bond cleavage and formation events. Control experiments provided important insights into the mechanism.*

Skeletal reorganization, a type of organic transformations featuring bond connectivity change of a framework, has appealed extensive interests from the synthetic community.[1] The fascinating features of these reactions lie in not only their capability of accessing complex and challenging target molecules from readily available starting materials, but also their thought-provoking mechanisms that typically involve multiple bond cleavage and formation steps.[1-4] Among the known skeletal reorganizations, those of alkynes, particularly cycloisomerizations of 1,n-enynes, are probably most explored.[2] Although sporadic examples are known for other functional groups, they are much less established.[3] Nevertheless, these extraordinary transformations have found wide applications in organic synthesis.[4] Herein, we introduce a new unusual skeletal reorganization of the less studied functionality, oxetane.

Due to the high ring strain of the four-membered ring, the most well-known reactivity of oxetane is ring-opening upon nucleophilic attack leading to C–O bond cleavage (Scheme 1a).[5,6] The other type is ring-expansion, for example, insertion with a carbene.[5,7] Other than these two straightforward patterns, new reactivity of oxetanes has been limitedly known. In this context, new reactivity study on this useful functional group is high desirable. The present study discloses a new example that leads to unusual change in bond connectivity (Scheme 1b). Our journey was initiated by the curiosity about the possible synthesis of indolines from oxetane-tethered anilines **1** (Scheme 1c). We hypothesized that the electron-rich arene might serve as a nucleophile to attack the oxetane ring upon suitable activation. However, to our surprise, 1,2-dihydroquinoline **2** was observed instead of the indoline product in the presence of a Lewis acid. The mechanistic ambiguity as well as its capability for rapid access to the important 1,2-dihydroquinoline heterocycle prompted us to further study this serendipitous discovery.[8,9]



***Scheme 1**.* Introduction to oxetane chemistry

Oxetane-tethered aniline **1a** was initially employed as the model substrate, in which a *meta*-hydroxy group was installed on the arene to enhance its nucleophilicity (Table 1). Various oxophilic Lewis acids were examined as catalyst. While AgOTf and La(OTf)$_3$ showed no catalytic activity (entries 1–2), Fe(OTf)$_3$, Sc(OTf)$_3$ and In(OTf)$_3$ were able to catalyze this process, albeit with moderate efficiency (entries 3–5). These reactions in dioxane solvent at 100 °C led to the formation of a mixture of two regioisomeric dihydroquinolines **2a** and **2a'**. The structure of **2a** was confirmed by X-ray crystallography (Figure 1). While some Brønsted acids were also evaluated, including TsOH and Tf_2NH, none of them resulted in the desired product formation. Among the effective catalysts, In(OTf)$_3$ proved superior, providing the highest yield and selectivity (entry 5). Other parameters, such as solvent and temperature, were examined in hope of improving the reaction efficiency. Unfortunately, these efforts were not fruitful. For example, the reactions in DCE or MeCN showed almost no reactivity (entries 6–7). Decreasing the temperature also resulted in lower reaction efficiency.

Aiming to further improve the reaction efficiency, we next examined different protective groups on the nitrogen atom. We reasoned that the electronic properties of these protective groups might remotely influence the reactivity of both the arene and oxetane motifs. Indeed, this influence was found to be dramatic (Table 2). When acetyl or benzoyl was used as the protective group, no reaction was observed under otherwise identical conditions (entries 1-2). Next, we resorted to fine tuning of the sulfonyl protective groups. Electron-withdrawing and electron-donating groups were installed on the *para*-position of the benzene sulfonyl group (entries 3-8). It was found that the reactivity varied, but the regioselectivity remained essentially the same. Among them, the *p*-

[*] Dr. H. Huang,[+] Prof. J. Sun
Jiangsu Key Laboratory of Advanced Catalytic Materials & Technology, School of Petrochemical Engineering, Changzhou University, Changzhou 213164, China

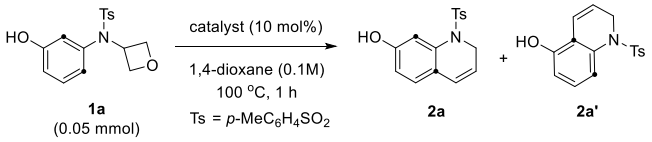
G. Wang,[+] Dr. W. Guo, C. Qian, Prof. J. Sun
Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong SAR, China
E-mail: sunjw@ust.hk

[+] These authors contributed equally to this work.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201xxxxxx.

10.1002/anie.201916727

Table 1: Condition Optimization



entry	catalyst	solvent	yield (%)[a]	2a/2a'[a]
1	AgOTf	1,4-dioxane	<5[b]	–
2	$La(OTf)_3$	"	<5[b]	–
3	$Fe(OTf)_3$	"	43[c]	2.3:1
4	$Sc(OTf)_3$	"	48[c]	1.3:1
5	$In(OTf)_3$	"	53[c]	2.9:1
6	"	DCE	<5[c]	–
7	"	MeCN	<5[d]	–

[a] Yield and ratio were based on analysis of the ^{1}H NMR spectrum of the crude mixture using CH_2Br_2 as an internal standard. [b] No reaction [c] Complete conversion. The remainder of the mass balance is a complex mixture. [d] Conversion < 20%.

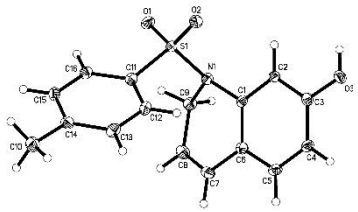
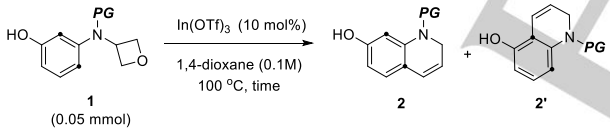
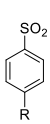


Figure 1. ORTEP structure of product **2a**.

Table 2: Evaluation of the protective group



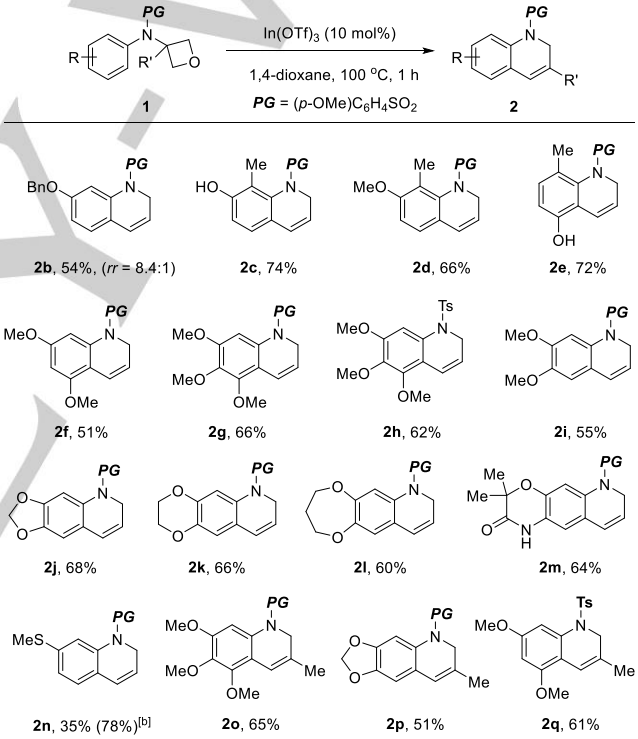
entry	*PG*		time (h)	yield (%)[a]	2/2'
1	Ac		6	<5[b]	–
2	Bz		6	<5[b]	–
3		R = Br	6	48	2.4:1
4		R = Cl	1	68	3.3:1
5		R = F	1	65	2.1:1
6		$R = NO_2$	6	39	2.9:1
7		R = Me (Ts)	1	53	2.9:1
8		R = OMe	1	70	2.9:1
9			6	56	3.0:1
10	2-$NpSO_2$		6	55	3.2:1
11	Ms ($MeSO_2$)		6	52	2.5:1

[a] Yield and ratio were based on analysis of the ^{1}H NMR spectrum of the crude mixture using CH_2Br_2 as an internal standard. [b] No reaction.

methoxybenzenesulfonyl group provided the highest efficiency (entry 8). Other sulfonyl groups could not further improve the reaction outcome (entries 9-11). Notably, the use of an *N*-alkyl group (e.g., Me) resulted in no reaction, presumably due to the increased coordination ability of this nitrogen, which led to catalyst deactivation and loss of amine nucleophilicity.

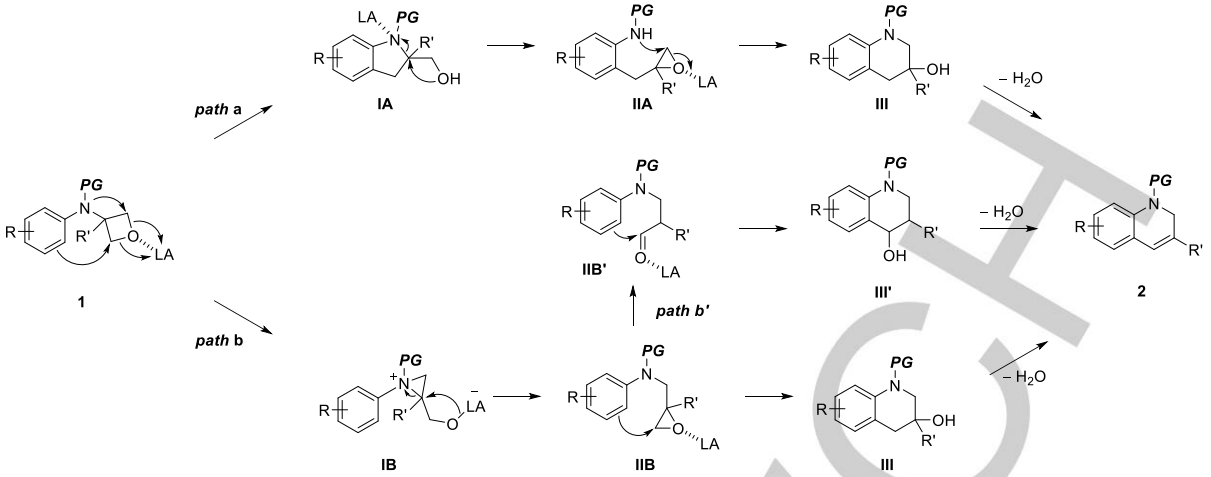
A range of variously substituted anilines bearing an *N*-oxetane motif were subjected to the standard conditions (Scheme 2). All of them underwent smooth skeletal reorganization to form the corresponding dihydroquinolines as the major products. Functional groups like ether, free hydroxy group, and amide, were tolerated. The reaction efficiency was generally good when electron-rich arene was used, which is consistent with the role of the arene as a nucleophile in this process. The presence of a methylsulphenyl group could also give the desired product **2n**, although the conversion was low due to competing binding of the sulfur with the catalyst. Finally, we also examined the reactivity of 3,3-disubstituted oxetanes (R' ≠ H). Gratifyingly, despite the increased steric hindrance, the desired 3-substituted 1,2-dihydroquinolines **2o**–**q** were obtained successfully. It is worth noting that the position of the R' substituent in the products provided additional support to the proposed mechanism (*vide infra*).

Scheme 2. Reaction Scope.[a]



[a] Reaction scale: **1** (0.2 mmol), $In(OTf)_3$ (0.02 mmol), solvent (2 mL). Isolated yield. *rr* = regioisomeric ratio. [b] Yield in parentheses is based on recovered starting material.

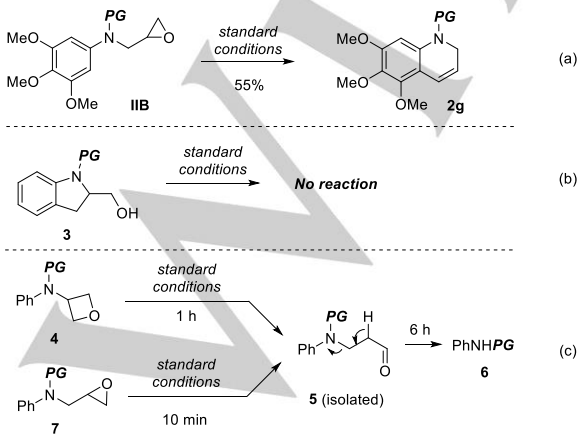
Two possible mechanisms are depicted in Scheme 3 to rationalize this unusual process. We believe that this reaction begins with Lewis acid activation of the oxetane functionality, which becomes susceptible to nucleophilic attack. In path *a*, the electron-rich arene serves as the nucleophile to open the oxetane ring, leading to indoline **IA**. This is the originally expected product, though not observed. Next, the Lewis acid catalyst activates the protected amine group, and the pendant hydroxy group undergoes nucleophilic substitution of the sulfonamide group to form epoxide **IIA**. Subsequent activation of the epoxide followed by nucleophilic ring-opening by the sulfonamide group results in formation of tetrahydroquinoline **III**. Further elimination of a water molecule leads to the observed product **2**. Alternatively, as shown in path *b*, the



Scheme 3. Proposed mechanisms.

nitrogen atom in sulfonamide may also serve as the nucleophile to open the oxetane ring, which forms aziridinium zwitterion **IB**. Due to the high ring-opening propensity of the aziridinium ion, an additional nucleophilic substitution takes place to form epoxide **IIB**. Subsequent reaction on this epoxide intermediate may bifurcate into two possibilities. Upon activation by the Lewis acid catalyst, the well-positioned epoxide might be attacked directly by the arene nucleophile to form **III**, the same intermediate in path *a*. It is also possible for the epoxide **IIB** to undergo a House–Meinwald rearrangement to form aldehyde **IIB′**,[10] which then cyclizes with the arene moiety to form tetrahydroquinoline **III′** (path *b*′). A similar dehydration leads to the same 1,2-hydroquinoline product **2**. Both paths involve multiple nucleophilic substitutions, which are key steps to achieve the bond connectivity change for skeletal reorganization.

To gain more insights into the mechanism, we carried out a series of control experiments. For example, we managed to synthesize the intermediate **IIB** and subjected it into the standard conditions. The corresponding 1,2-dihydroquinoline **2g** was obtained in 55% yield (Scheme 4a), indicating that this intermediate is chemically competent and thus it is consistent with path *b*. To further probe the chemical competence of intermediate **IA** in path *a*, we also prepared indoline **3**. However, under the standard conditions, indoline **3** did not show any reactivity (Scheme 4b), which rules out path *a*. To help understand the detailed steps in path *b*, substrate **4** was prepared and subjected to the standard conditions. Indeed,

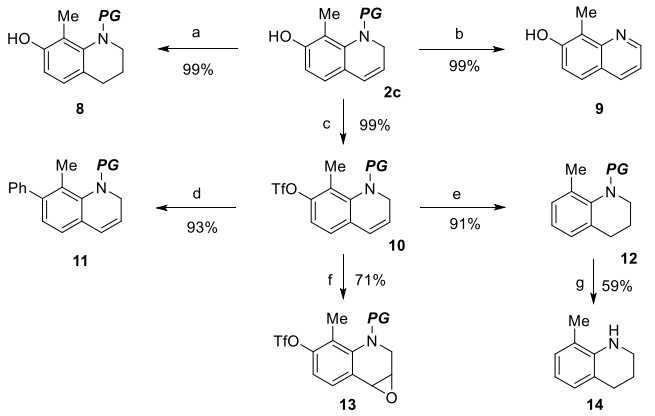


Scheme 4. Control experiments. ***PG*** = (*p*-OMe)$C_6H_4SO_2$.

aldehyde **5** was isolated and fully characterized. Since the benzene ring here is not nucleophilic enough, aldehyde **5** gradually underwent decomposition to form sulfonamide **6** via *retro*-Michael addition (Scheme 4c). However, epoxide **7** was not dected in this process. We believe that this is due to the fast consumption of **7** (vs. its formation) that prevented its acummulation. Nevertheless, to further substantiate the House–Meinwald rearrangement step from epoxide **IIB** to aldehyde **IIB'**, we separately prepared epoxide **7** and subjected it to the standard conditions. As expected, it only took 10 min for its conversion to aldehyde **5**, indicating this step is very facile. Taken together, path *b′* involving the epoxide and aldehyde intermediates is most consistent with these experimental results.

The 1,2-dihydroquinoline products are useful precursors to other nitrogen heterocycles. We carried out some derivatizations of product **2c** (Scheme 5). For example, simple hydrogenation catalyzed by Pd/C led to quantitative formation of tetrahydroquinoline **8**. Furthermore, base-promoted desulfonylative elimination gave the corresponding quinoline **9** in excellent yield. Moreover, after triflation, the hydroxy group in the arene motif could be either used for cross-coupling to form **11** or removed to form **12** via triflate **10**. The double bond in triflate **10** could be further oxidized to epoxide **13** efficiently. Finally, the sulfonyl group could also be successfully removed to form the free 1,2,3,4-tetrahydroquinoline **14**. All these transformations are straightforward and highly efficient.

In summary, we have discovered a new skeletal reorganization process of oxetanes. It represents an unprecedented reactivity pattern of the oxetane functional group. In the presence of $In(OTf)_3$ as catalyst, a range of oxetane-tethered electron-rich anilines altered their normal reactivity (from the originally designed indoline products) to undergo a series of bond cleavage and formation steps, leading to the unexpected 1,2-dihydroquinoline products. This process also provides expedient access to these useful heterocycles and their derivatives. Of particular note is the intriguing mechanism. While two plausible paths were proposed, a series of control experiments provided important insights to rule out the one with initial arene attack and further substantiated the one with nitrogen attack on the oxetane. The intermediacy of an epoxide and its rearranged aldehyde intermediate was also consistent with the control experiments. This study also alluded that other new transformations may be discovered by intercepting these intermediates starting from properly designed oxetane substrates.



Scheme 5. Product transformations. [a] Pd/C, H_2, EtOAc, RT. [b] NaOH, EtOH, 100 °C. [c] Tf_2O, pyridine, DCM, RT. [d] $PhB(OH)_2$, $Pd(PPh_3)_2Cl_2$, Cs_2CO_3, 1,4-dioxane, H_2O, reflux. [e] Mg, Pd/C, NH_4OAc, MeOH, RT. [f] *m*CPBA, DCM, RT. [g] Na/naphthalene, DME, -50 °C. *PG* = (*p*-OMe)$C_6H_4SO_2$.

Acknowledgements

Financial support was provided by NSFC (21572192, 91956114) and Hong Kong RGC (16302318) and Jiangsu specially appointed professors program. We also thank Dr. Dengke Ma and Dr. Renwei Zhang for helpful discussion and Dr. Herman Sung for assistance in structural determination.

Keywords: strained molecules • nitrogen heterocycles • rearrangement • oxetane • cyclization

[1] a) "Skeletal Rearrangement Reactions": I. Nakamura in *Transition-Metal-Mediated Aromatic Ring Construction* (Ed.: K. Tanaka), Wiley, New Jersey, 2013, pp. 743–771; b) X. Xie, L. Zu, *Synlett* **2018**, *29*, 1008-1013.

[2] Selected reviews (a–c) and examples (d–l) on skeletal reorganization of alkynes, such as enyne cycloisomerization: a) C. Aubert, O. Buisine, M. Malacria, *Chem. Rev.* **2002**, *102*, 813–834; b) L. Zhang, J. Sun, S. A. Kozmin, *Adv. Synth. Catal.* **2006**, *348*, 2271–2296; c) M. Tobisu, N. Chatani, *Chem. Soc. Rev.* **2008**, *37*, 300–307; d) N. Chatani, H. Inoue, T. Kotsuma, S. Murai, *J. Am. Chem. Soc.* **2002**, *124*, 10294–10295; e) V. Mamane, T. Gress, H. Krause, A. Fürstner, *J. Am. Chem. Soc.* **2004**, *126*, 8654–8655; f) G. Zhang, V. J. Catalano, L. Zhang, *J. Am. Chem. Soc.* **2007**, *129*, 11358–11359; g) J.-M. Tang, S. Bhunia, S. M. A. Sohel, M.-Y. Lin, H.-Y. Liao, S. Datta, A. Das, R.-S. Liu, *J. Am. Chem. Soc.* **2007**, *129*, 15677–15683; h) K. Ota, S. I. Lee, J.-M. Tang, M. Takachi, H. Nakai, T. Morimoto, H. Sakurai, K. Kataoka, N. Chatani, *J. Am. Chem. Soc.* **2009**, *132*, 15203–15211; i) I. Nakamura, D. Zhang, M. Terada, *J. Am. Chem. Soc.* **2010**, *132*, 7884–7886; j) J. Barluenga, E. T.udela, R. Vicente, A. Ballesteros, M. Tomás, *Angew. Chem. Int. Ed.* **2011**, *50*, 2107–2110; k) T. Matsuda, T. Goya, L. Liu, Y. Sakurai, S. Watanuki, N. Ishida, M. Murakami, *Angew. Chem. Int. Ed.* **2013**, *52*, 6492–6495; l) B. Zhou, L. Li, X.-Q. Zhu, J.-Z. Yan, Y.-L. Guo, L.-W. Ye, *Angew. Chem. Int. Ed.* **2017**, *56*, 4015–4019.

[3] Selected examples on skeletal reorganization of other functionalities: a) d) T.-P. Loh, Q.-Y. Hu, K.-T. Tan, H.-S. Cheng, *Org. Lett.* **2001**, *3*, 2669–2672; b) J. M. Ndungu, K. L. Larson, R. Sarpong, *Org. Lett.* **2005**, *7*, 5845–5848; c) S. Álvarez, G. Domínguez, A. Gradillas, J. Pérez-Castells, *Eur. J. Org. Chem.* **2013**, 3094–3102; d) H. Zhang, C. Li, G. Xie, B. Wang, Y. Zhang, J. Wang, *J. Org. Chem.* **2014**, *79*, 6286–6293; e) N. Wang, Q.-S. Gu, Z.-L. Li, Z. Li, Y.-L. Guo, Z. Guo, X.-Y. Liu, *Angew. Chem. Int. Ed.* **2018**, *57*, 14225–14229.

[4] Applications of skeletal reorganization in natural product synthesis: a) A. Saitman, P. Rulliere, S. D. E. Sullivan, E. A. Theodorakis, *Org. Lett.* **2011**, *13*, 5854–5857; b) O. Wagnieres, Z. Xu, Q. Wang, J. Zhu, *J. Am. Chem. Soc.* **2014**, *136*, 15102–15108; c) X.-M. Zhang, Y.-Q. Tu, F.-M. Zhang, Z.-H. Chen, S.-H. Wang, *Chem. Soc. Rev.* **2017**, *46*, 2272–2305; d) J. R. Hanson, *J. Chem. Res.* **2018**, *42*, 175–180; e) D. K. Singh, I. Kim, *J. Org. Chem.* **2018**, *83*, 1667–1672.

[5] For leading reviews on oxetane chemistry, see: a) J. A. Burkhard, G. Wuitschik, M. Rogers-Evans, K. Müller, E. M. Carreira, *Angew Chem. Int. Ed.* **2010**, *49*, 9052–9067; b) D. J. Mack, J. T. Njardarson, *ACS Catal.* **2013**, *3*, 272-286; c) Z. Wang, Z. Chen, J. Sun, *Org. Biomol. Chem.* **2014**, *12*, 6028–6032; d) C. A. Malapit, A. R. Howell, *J. Org. Chem.* **2015**, *80*, 8489–8495; e) J. A. Bull, R. A. Croft, O. A. Davis, R. Doran, K. F. Morgan, *Chem. Rev.* **2016**, *116*, 12150–12233.

[6] a) M. Mizuno, M. Kanai, A. Iida, K. Tomioka, *Tetrahedron: Asymmetry* **1996**, *7*, 2483–2484; b) R. N. Loy, E. N. Jacobsen, *J. Am. Chem. Soc.* **2009**, *131*, 2786–2787; c) J. A. Burkhard, B. H. Tchitchanov, E. M. Carreira, *Angew. Chem. Int. Ed*. **2011**, *50*, 5379–5382; d) S. A. Ruider, S. Müller, E. M. Carreira, *Angew. Chem. Int. Ed*. **2013**, *52*, 11908–11911; e) A. R. White, R. A. Kozlowski, S.-C. Tsai, C. D. Vanderwal, *Angew. Chem. Int. Ed*. **2017**, *56*, 10525–10529; For our own efforts: f) W. Zhao, Z. Wang, J. Sun, *Angew. Chem. Int. Ed*. **2012**, *51*, 6209–6213; g) Z. Chen, B. Wang, Z. Wang, G. Zhu, J. Sun, *Angew. Chem., Int. Ed*. **2013**, *52*, 2027–2031; h) Z. Wang, Z. Chen, J. Sun, *Angew. Chem., Int. Ed*. **2013,** *52*, 6685–6688; i) W. Yang, J. Sun, *Angew. Chem. Int. Ed.* **2016**, *55*, 1868–1871; j) W. Yang, Z. Wang, J. Sun, *Angew. Chem. Int. Ed*. **2016**, *55*, 6954–6958; k) R. Zhang, W. Guo, M. Duan, K. N. Houk, J. Sun, *Angew. Chem. Int. Ed*. **2019**, *58*, 18055–18060; l) H. Huang, W. Yang, Z. Chen, Z. Lai, J. Sun, *Chem. Sci.* **2019**, *10*, 9586–9590.

[7] a) H. Nozaki, S. Moriuti, H. Takaya, R. Noyori, *Tetrahedron Lett.* **1966**, 43, 5239–5244; b) T.-Y. Y. Gu, W. P. Weber, *J. Am. Chem. Soc.* **1980**, *102*, 1641–1644; c) K. Ito, T. Katsuki, *Chem. Lett.* **1994**, 1857–1860; d) M. M.-C. Lo, G. C. Fu, *Tetrahedron* **2001**, *57*, 2621–2634; e) D. Rix, R. Ballesteros-Garrido, W. Zeghida, C. Besnard, J. Lacour, *Angew. Chem. Int. Ed*. **2011**, *50*, 7308–7311; f) C. Gronnier, S. Kramer, Y. Odabachian, F. Gagosz, *J. Am. Chem. Soc.* **2012**, *134*, 828–831; g) B. Guo, G. Schwarzwalder, J. T. Njardarson, *Angew. Chem. Int. Ed*. **2012**, *51*, 5675–5678; h) Q. Yin, S.-L. You, *Org. Lett.* **2014**, *16*, 1810–1813; i) J. Rintjema, W. Guo, E. Martin, E. C. Escudero-Adan, A. W. Kleij, *Chem. Eur. J.* **2015**, *21*, 10754–10762; j) Y.-N. Wang, L.-C. Yang, Z.-Q. Rong, T.-L. Liu, R. Liu, Y. Zhao, *Angew. Chem. Int. Ed*. **2018**, *57*, 1596–1600; k) H. Xu, S. Khan, H. Li, X. Wu, Y. J. Zhang, *Org. Lett.* **2019**, *21*, 214–217.

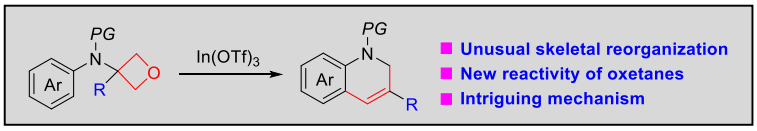
[8] a) L. M. Nainwal, M. M. Alam, *Eur. J. Med. Chem.* **2019**, *164*, 121–170; b) N. J. Victor, R. Sakthivel, K. M. Muraleedharan, D. Karunagaran, *ChemMedChem*, **2013**, *8*, 1623–1628; c) S. Duggirala, J. V. Napoleon, R. P. Nankar, V. S. Adeeba, M. K. Manheri, M. Doble, *Eur. J. Med. Chem.* **2016**, 123, 557–567; d) H. Takahashi, Y. Bekkali, A. J. Capolino, T. Gilmore, S. E. Goldrick, R. M. Nelson, D. Trenzio, J. Wang, L. Zuvela-Jelaska, J. Proudfoot, G. Nabozny, D. Thomson, *Bioorg. Med. Chem. Lett.* **2006**, *16*, 1549–1552.

[9] For selected other methods for the synthesis of 1,2-dihydroquinolines: a) Y. Luo, Z. Li, C.-J. Li, *Org. Lett.* **2005**, *7*, 2675–2678; b) X. Liu, Y. Liu, *Org. Biomol. Chem.* **2010**, *8*, 4063–4065; c) C. Zhu, S. Ma, *Angew. Chem. Int. Ed*. **2014**, *53*, 13532–13535; d) D, Ding, T. Mou, M. Feng, X. Jiang, *J. Am. Chem. Soc.* **2016**, *138*, 5218–5221; e) R. Kuppusamy, R. Santhoshkumar, R. Boobalan, H.-R. Wu, C.-H. Cheng, *ACS Catal.* **2018**, *8*, 1880–1883.

[10] a) H. O. House, *J. Am. Chem. Soc.* **1955**, *77*, 3070–3075; b) J. Meinwald, S. S. Labana, M. S. Chadha, *J. Am. Chem. Soc.* **1963**, *85*, 582–585.

10.1002/anie.201916727

Entry for the Table of Contents



An unusual skeletal reorganization of oxetanes is described, in which oxetane-tethered anilines reacted unexpectedly to form 1,2-dihydroquinolines in the presence of $In(OTf)_3$ as catalyst. This process proceeds via an intriguing mechanism involving a series of bond cleavage and formation steps.