EurJOC
European Journal of Organic Chemistry

A Journal of ChemPubSoc Europe

Accepted Article

Title: Chlorotropylium promoted conversions of oximes to amides and nitriles

Authors: Jiaxi Xu, Yu Gao, Zhenjiang Li, Jingjing Liu, Tianfo Guo, Lei Zhang, Haixin Wang, Zhihao Zhang, and Kai Guo

To be cited as: *Eur. J. Org. Chem.* 10.1002/ejoc.201901537

Link to VoR: http://dx.doi.org/10.1002/ejoc.201901537

Supported by ACES Asian Chemical Editorial Society

WILEY-VCH

Chlorotropylium promoted conversions of oximes to amides and nitriles

Dr. Jiaxi Xu, Dr. Yu Gao, Prof. Dr. Zhenjiang Li*, Dr. Jingjing Liu, Dr. Tianfo Guo, Lei Zhang, Dr. Haixin Wang, Zhihao Zhang and Prof. Dr. Kai Guo*

State Key Laboratory of Materials-Oriented Chemical Engineering, College of Biotechnology and Pharmaceutical Engineering, Nanjing Tech University, 30 Puzhu Road South, Nanjing 211816, China;

Corresponding Author

Kai Guo and Zhenjiang Li; E-mail: guok@njtech.edu.cn; zjli@njtech.edu.cn. Tel +86 25 5813 9926; Fax +86 25 5813 9935.

Abstract

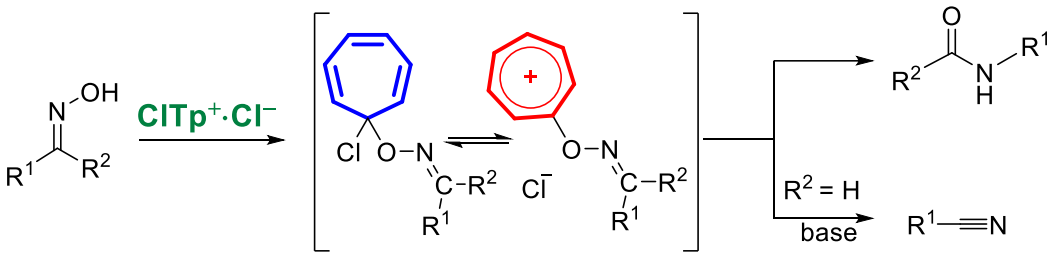
Chlorotropylium chloride as trigger/catalyst promoted transformations of oximes of ketones and aldehydes to their corresponding amides and nitriles in excellent yields (up to 99%) by short reaction times (mostly 10–15 min). Oximes were attacked electrophilically on the hydroxyl oxygen by chlorotropylium, the produced tropylium oxime ethers were the key intermediates, of which the ketoxime ether led to amide via Beckmann rearrangement, and the aldoxime ether led to nitrile via nitrogen base DBU assisted formal dehydration. This chlorotropylium activation protocol offered general, mild, and efficient avenues bifurcately from oximes to both amides and nitriles by one organocatalyst.

Keywords

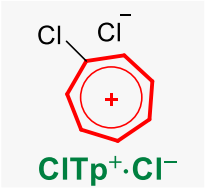
Amides; Organocatalysis; Rearrangement; Oximes; Tropylium

10.1002/ejoc.201901537

Graphic Abstract



- Broad substrates
- High yields (up to 99%)
- Short reaction time
- Mechanistic insights



Introduction

Cycloheptatrienylium (tropylium) ion was one of the most stable carbocations that was firstly prepared in a form of tropylium bromide by Doering in 1954.[1] Tropylium ion possessed aromaticity and showed remarkable stability due to its 6π-electron structure that obeying Hückel's [4n + 2] rule.[2] Since Doering's pioneering work on the highly stable tropylium that ushered non-benzenoid aromatics chemistry,[3] series of derivatives of tropylium,[4-8] together with its minimal analog non-benzenoid cyclopropenylium cation (cyclopropenium ion),[9, 10] in which n = 0, constantly attracted interests in both theoretical[11] and synthetic organic chemistry[12, 13]. In exploring stable carbocations[14] in promoting or catalyzing organic reactions, triarylmethyliums emerged as Lewis acidic catalysts[15-20] recently; in parallel, another two types of stable carbocations, cyclopropenium and tropylium (Figure 1), were promising in mediating/catalyzing organic transformations via both the Lewis acidity of the carbenium carbon centers and the aromaticity[6, 21] of the non-benzenoid aromatic rings.

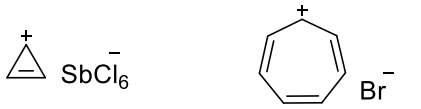
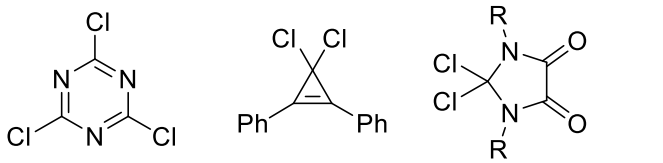


Figure 1. Two non-benzenoid carbocyclic aromatic ions, cyclopropenium and tropylium.

Despite being the 'first bottled' stable carbocation,[14] tropylium and its analog ions have rarely been applied in practical synthetic practice[9, 22-24] until Lambert disclosed the first tropylium mediated α-cyanation of amines[25]. Inspired by an insightful mechanism of dearomatization/rearomatization steps suggested by Lambert in *gem*-dichlorocyclopropene furnished nucleophilic substitutions[25-28], Nguyen proposed dichlorocycloheptatriene promoted nucleophilic substitutions that underwent first catalytic tropylium mechanism[29-32].

Oxime undergoes Beckmann rearrangement[33] that constructed amide linkage[34] vital to lactam production and provided monomers to nylon industries, i.e. for nylon 6 and nylon 12.[35, 36] Beckmann rearrangement usually promoted by acidic catalysts[33, 35] such as in the application of

fuming sulfuric acid and sulfonic acids in commercial routes, however, mild and tolerant organic catalysis in oxime transformations[37-47] were flourished (Figure 2) since Ishihara and Yamamoto disclosed the first organocatalyzed Beckmann rearrangement[48].

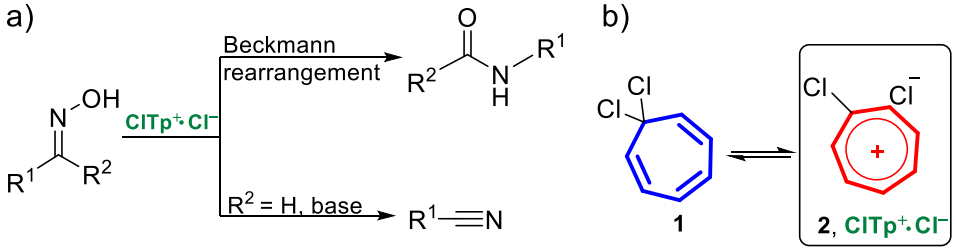


The first organocatalyst example[48] | Lambert[47] and Yadav[46] | Our previous work[42]

Figure 2. The typical regents in organo-catalyzed Beckmann rearrangements.

In contrast to the rearrangements of aldoximes to primary amides[49] or direct dehydration of aldoximes to nitriles[50-53], rare example[54] demonstrated organocatalytic transformations of aldoximes to nitriles without dehydration nor lead to primary amides. Based on our previous works on organocatalytic Beckmann rearrangement[42] and Swern-type oxidation[26] that were governed by aromaticity of the *gem*-dichloro compounds catalysts, we were interested in transformations of oximes of ketones and aldehydes to their corresponding amides and nitriles under promotion of chlorotropylium chloride ($ClTp^{+}\cdot Cl^{-}$)[32, 55, 56] (Scheme 1).

Scheme 1. Chlorotropylium chloride in promoting transformations of oximes to amides and nitriles.

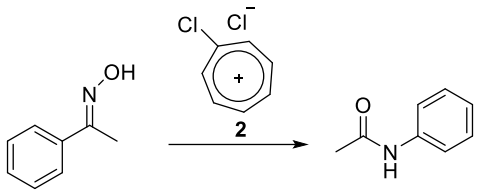


(a) Transformations of oximes of ketones and aldehydes to their corresponding amides and nitriles under promotion of chlorotropylium chloride ($ClTp^{+}\cdot Cl^{-}$). (b) The reversible isomerization between 7,7-dichlorocyclohepta-1,3,5-triene (**1**, $C_7H_6Cl_2$) and chlorotropylium chloride (**2**, $ClC_7H_6^{+}\cdot Cl^{-}$, $ClTp^{+}\cdot Cl^{-}$); reversal formation of dichlorocyclohepta-1,3,5-trienes from **2** would produce four isomers which were detailed in Scheme S1.

Results and Discussion

Beckmann rearrangement[49, 57-60] was triggered *via* heterolysis of the N–O bond in the oxime where an electrophile activated the oxime function. The seemingly straight forward protic acid catalysis mechanism[33] was later revealed much more sophisticated[61-64]. Considering the electrophilic nature of chlorotropylium ($ClTp^+$) at the carbenium center, we firstly explored the activation potential of the $ClTp^+ \cdot Cl^-$ (**2**) in effecting the Beckmann rearrangements (Table 1).

Table 1. The optimization of the Beckmann rearrangement reaction conditions.[a]



3a **4a**

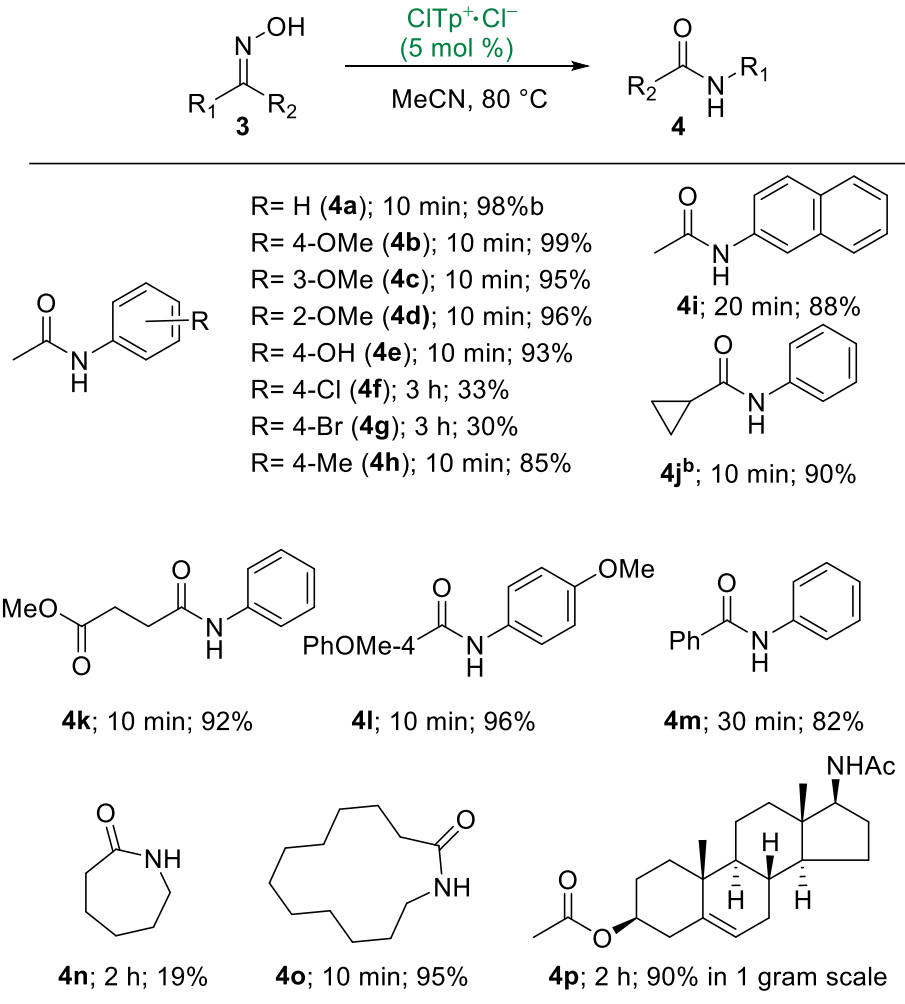
Entry	Solvent	**2** (mol%)	T/°C	Time/min	yield/%[b]
1	MeCN	10	rt	120	40
2	MeCN	10	80	10	99
3	MeCN	5	80	10	98
4	MeCN	1	80	60	80
5	Toluene	5	80	30	60
6	DMF	5	80	30	30
7	$MeNO_2$	5	80	120	23
8	1,4-dioxane	5	80	120	0
9	THF	5	66	30	13
10	DCE	5	83	30	90
11	MeCN	0	80	120	0
12[c]	MeCN	0 (5%)[c]	80	120	0

[a] 1 mmol of the acetophenone oxime **3a** in solvent (5 mL). [b] isolated yields. [c] HCl (36−38 wt %, 5 mol%) was added in place of **2** in promoting the reaction.

Acetophenone oxime (**3a**) was selected as a model substrate for the preliminary examination of the performance of chlorotropylium chloride in promoting the reactions. Series trial reactions to screen the optimal conditions were shown in Table 1. Substoichiometric amount (10 mol %) of $ClTp^+ \cdot Cl^-$ (**2**) in acetonitrile (MeCN) promoted transformation of acetophenone oxime (**3a**) to *N*-phenylacetamide (**4a**) by 40 % yield (Table 1, entry 1) at room temperature by 2 h. Raising the

temperature to reflux of the solvent (80 °C) received quantitative yield (99%) in remarkably short reaction time of 10 min (entry 2). Lower loading of chlorotropylium chloride at 5% and 1% (entries 3 and 4) showed excellent yields of 98% (by 10 min) and 80% (by 60 min), respectively. Encouraged by the promising results, common nonprotic organic solvents were screened by 5% of **2** at 80 °C (entries 5–8) or around their corresponding boiling temperatures (entries 9 and 10). Ethers resulted unfavorable yields (entries 8 and 9), however, toluene and 1,2-dichloroethane (DCE) (entries 5 and 10) exhibited good to excellent outcomes by 30 min.

Scheme 2. Generality and scope of chlorotropylium chloride promoted Beckmann rearrangement.[a]



[a] Reactions were performed with 1 mmol of **3** in MeCN (5 mL). Isolated yield. [b] The oxime **3j** was formed as mixtures of E/Z isomers (4:1).

To exclude background reactions, blank control without **2** (entry 11) revealed no conversion

of the substrate **3a**. Possibility of the byproduct HCl in promoting the rearrangement (*vide infra*, Scheme 4) was ruled out by using 5% of hydrochloric acid (entry 12) in place of **2**, no rearrangement of **3a** was observed. Hence, optimal conditions of $ClTp^{+}\cdot Cl^{-}$ (**2**) at 5% loading in reflux MeCN (80 °C) were employed in the following Beckmann rearrangements.

The scope and limitation of chlorotropylium chloride in activating Beckmann rearrangement was explored by testing typical ketoximes as the substrates under the optimal conditions (Scheme 2). It was exciting that arrays of aromatic and aliphatic ketoximes were converted smoothly to the corresponding amides in good to excellent yields (up to 99%). Acetophenone oximes with electron-donating groups, including methoxy (**3b−3d**), hydroxyl (**3e**), and methyl (**3h**) on the phenyl ring, all offered the corresponding acetanilides in excellent yields within 10 min.

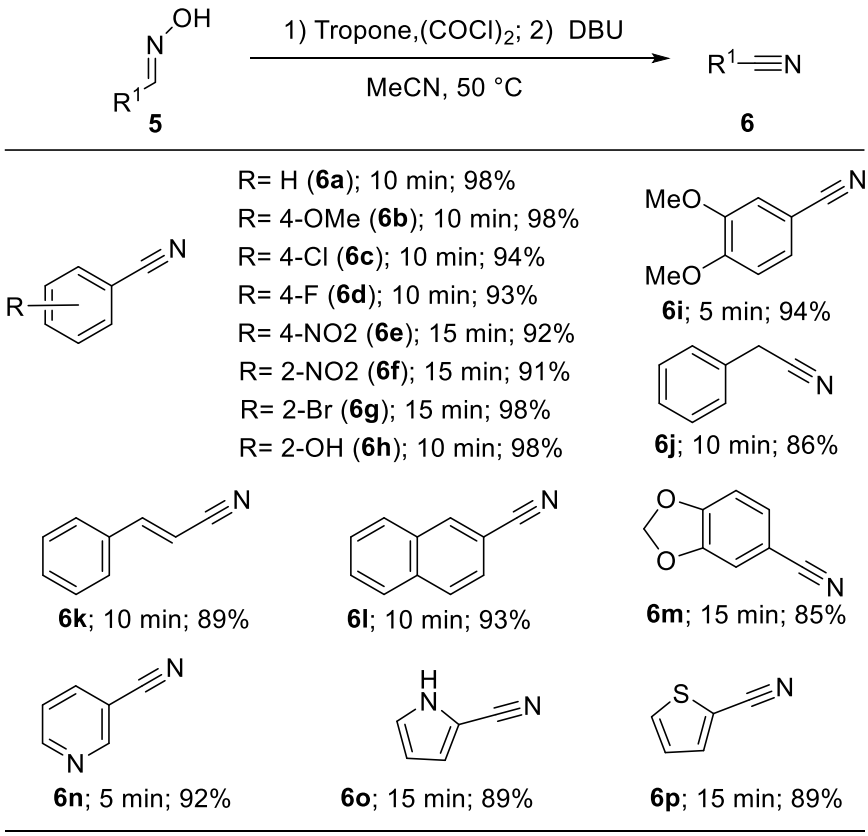
Acetophenone oximes with electron-withdrawing groups were also conductive under this protocol. N-(4-Chlorophenyl)acetamide (**4f**) and N-(4-bromophenyl)acetamide (**4g**) were obtained in 33% and 30% yields by 3 h. Furthermore, 2-acetonaphthone oxime **3i** featuring an aromatic fused ring was amenable to furnishing its rearranged product **4i** with 88% yield in 20 min. In conjunction with methyl, several diversified R^2 groups of oximes **3**, including cyclopropyl (**3j**), an aliphatic chain (R^2 = $MeCO_2(CH_2)_2$−, **3k**) and phenyl (**3m**), were studied and engaged in the rearrangements with high yields. One exemplar symmetrical ketoxime **3l** was converted into amides **4l** with 96% yields in 10 min.

Commercial relevant oximes were evaluated under the promotion of chlorotropylium chloride. 4-Acetaminophenol **4e**, that is active pharmaceutical ingredient to Paracetamol, received 93% yield in 10 min. Two aliphatic cyclic oximes **3n** and **3o**, which were precursors to nylon 6 and nylon 12, showed sharp contrast. Cyclohexyl oxime **3n** failed to obtain acceptable yield (19% by 2 h) of ε-caprolactam **4n**, notwithstanding, cyclododecyl oxime **3o** was rearranged into the target ω-laurolactam **4o** by 95% yield in 10 min. Finally, to leverage chlorotropylium chloride activation strategy, we examined its workability in a complex substrate oxime of pregnenolone acetate (Scheme 2, **3p**). One gram of **3p** was successfully converted into amide **4p** in 90% yield by 2 h.

We conducted the reaction E : Z mixture of (4-hydroxyphenyl)(phenyl)methanone oxime (**3q**) (1.5 : 1) under these heating reaction condition in Figure S2. As expected, exclusive transmigration was observed, leading to a 1.5 : 1 mixture of amide products in 80% yield. This result suggests that oxime isomerization does not occur under these reaction conditions.

Intrigued by this chlorotropylium chloride promoted Beckmann rearrangement of ketoxime, we were interested in aldoximes as substrates under the conditions. To our surprise, no primary amide usually viable from Beckmann rearrangement of aldoxime[65] was observed, nor dehydration of aldoximes to nitriles[51, 52] were detected. To obviate ordinary routes to nitrile[66] by harsh dehydration steps, we turned our exploration to chlorotropylium chloride furnished cleavage of the N–O bond in aldoxime that would be facilitated by a precedent proton abstraction step[53] by Brønsted bases.

Scheme 3. Generality and scope of chlorotropylium chloride promoted aldoximes to nitriles.[a]



[a] Reactions were performed with 2 mmol of **5** in MeCN (10 mL), aldoxime **5** (1.0 equiv.), tropone (1

mol%), $(COCl)_2$ (1.0 equiv.), and DBU (3.0 equiv.); isolated yields.

Benzaldoxime (**5a**) was selected as a model substrate to optimize the reaction conditions (Table S1). Evaluations in terms of Brønsted bases, ratios of base to **5a**, solvents, reaction temperatures, the loading of the precatalyst tropone were performed. Optimal conditions revealed 3 equiv. of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) base in MeCN solvent at 50 °C under the catalysis of 1 mol% of tropone and 1 equiv. of oxalyl chloride commenced transformation of **5a** to nitrile **6a** by quantitative yield in 10 min. Broad scope of the chlorotropylium chloride catalyzed transformations of aldoximes to nitriles were verified (Scheme 3) in aromatic, heteroaromatic, and aliphatic aldoximes substrates by excellent to quantitative yields between 5 to 15 min.

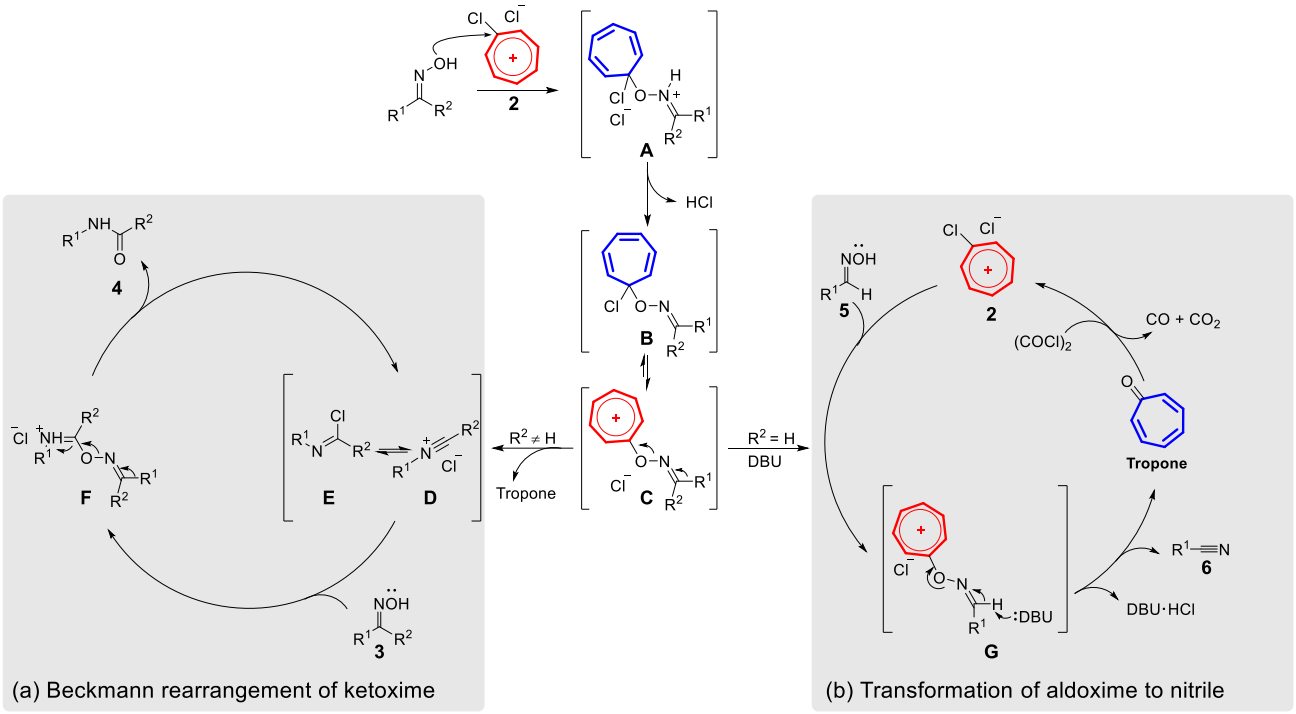
Plausible mechanisms of oxime activations by chlorotropylium chloride were proposed base on our previous understanding of *gem*-dichloro compounds catalyzed/promoted reactions[26, 42] and seminal works in organocatalyzed Beckmann rearrangements. [39, 40, 44, 47, 67] The activations were commenced from a common intermediate **A** (Scheme 4), it was an oxime ether produced from the nucleophilic attack of chlorotropylium ($ClTp^+$) to oxygen of the hydroxyl in ketoxime **3** or aldoxime **5**. Spontaneous elimination of a molecule of HCl from **A** afforded intermediate **B**, then **B** released a chloride anion and delivered the key tropylium oxime ether **C**.

In a Beckmann rearrangement cycle (Scheme 4**, a**), where the R^2 group was alkyl or aryl rather than a hydrogen H ($R^2 \neq H$), R^1 migrated to N atom synchronized by cleavage of O–N bond compensated by carbonyl C=O formation in the released tropone. The intermediate nitrilium ion **D**, in equilibrium with its isomer imidoyl chloride **E**, would be attacked by ketoxime **3** on the nitrilium carbon to form a dimer-like cation **F**. Intermediate **E** was regenerated in accompany to a release of the product amide **4**. The **D**/**E** isomers were retrieved to undergo the self-propagating cycles independent of the chlorotropylium.

A counterpart aldoxime to nitrile cycle (Scheme 4**, b**) was proposed. Aldoxime was not able to be converted to nitrile or primary amide by simply addition of chlorotropylium chloride, albeit

tropylium aldoxime ether **G** was produced. Nitrogen base DBU abstracted a proton from **G** that effected collapse of oxime ether moiety to carbon–nitrogen triple bond (C≡N) in product nitrile **6** accompanied by expel of the precatalyst tropone. Equivalent amount of oxalyl chloride reacted with tropone that regenerated chlorotropylium chloride **2** *in situ* which will be engaged in the catalytic cycles.

Scheme 4. Bifurcate mechanisms of oximes to amides and nitriles from common intermediates **A**, **B**, and **C**. (a) Beckmann rearrangement of ketoxime to amide triggered by catalytic amount of chlorotropylium chloride **2**, the key role of intermediate **F** in the self-propagating cycle was validated[68]; (b) Chlorotropylium chloride catalyzed cleavage of O–N bond in aldoxime assisted by DBU base effected deprotonation, oxalyl chloride was used to regenerate chlorotropylium chloride from tropone *in situ*.



Conclusion

In conclusion, we firstly reported chlorotropylium chloride ($ClTp^{+}\cdot Cl^{-}$) as trigger/catalyst in transformations of oximes of ketones and aldehydes to their corresponding amides and nitriles in high efficiency under mild conditions. This protocol provided rapid access to amides and nitriles in minutes by excellent to quantitative yields. Seventeen amides and sixteen nitriles were

rapidly synthesized by chlorotropylium protocol in short time (mostly 10-15 min) with excellent yield (mostly > 90%). Bifurcate mechanisms from tropylium oxime ethers to amides via Beckmann rearrangement, and to nitriles via formal dehydration by one organocatalyst were proposed. The present study expanded the scope of tropylium catalysis and hopefully amenable to wider organocatalysis applications.

Experimental Section

General Remarks

All reactions were conducted with magnetic stirring under argon atmosphere in oven-dried glassware. Reagents were available from commercial suppliers and used without further purification unless otherwise noted. All of solvents in the reactions were distilled from proper drying reagents before using. All the oxime substrates used in this paper were prepared by the procedure which refluxing a mixture of 1.0 equiv of the corresponding aldehydes or ketones, 2.0 equiv of sodium acetate, and 1.5 equiv of hydroxylamine hydrochloride in aqueous ethyl alcohol. These oximes are mostly E form unless otherwise specified.

^{1}H NMR and ^{13}C NMR spectra were conducted on Bruker AV 300 or AV 400 MHz instruments in $CDCl_3$ with chemical shifts reported relative to a residual deuterated solvent as the internal standard. High-resolution mass spectra were experimented on Agilent Q-TOF 6520 mass spectrometer using electron spray ionization (ESI) as the ion source. Gas chromatograms were performed on an Agilent 7890A instrument using an Agilent DB-WAXETR column (30 m × 0.320 mm × 0.25 μm). Melting points in degrees Celsius(°C) were tested by Shanghai Precision & Scientific capillary melting point apparatus without corrected.

General procedure A for transformation of ketoximes to amides

To a solution of tropone (5.3 mg, 0.05 mmol) in dry acetonitrile (1 mL) was added oxalyl chloride (6.35 mg, 0.05 mmol) by dropwise. And the reaction mixture was stirred at room temperature with gas emission ceased. After 15 min, a solution of ketoxime **3** (1 mmol) in dry acetonitrile (4 mL) was added to the mixture by dropwise. The reaction solution was heated at

80°C under a nitrogen atmosphere for the appropriate time (see Scheme 2). After monitoring of the reaction for the completion by TLC, the organic solvent was removed by vacuum. Then the crude products were purified by silica gel column chromatography (PE/EA) to give the corresponding amide **4**. The structure of the compound **4** was confirmed by their mp, TLC, ^{1}H NMR, and ^{13}C NMR data.

General procedure B for transformation of aldoximes to nitriles

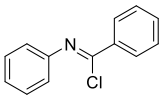
To a solution of aldoxime **5** (2 mmol) in a flame-dried Schlenk tube was added tropone (1 mol%) in acetonitrile (8 mL). A solution of $(COCl)_2$ (2 mmol) added to the mixture over 15 min by using a syringe pump. After the slow addition of DBU (6 mmol) in acetonitrile (2 mL), the reaction was heated at 50°C for the specified time (see Scheme 3). Monitoring completion of the reaction by TLC, the mixture was diluted with DCM and washed with water. The organic layer was dried with Na_2SO_4 and evaporated under reduced pressure to give the crude product. The pure product **6** was obtained from the crude product purified by flash chromatography (PE/EA). The structure of the compound **6** was confirmed by their mp, TLC, ^{1}H NMR and ^{13}C NMR data.

References

1. W. Von E. Doering and L. Knox, *J. Am. Chem. Soc.*, 1954, **76**, 3203-3206.
2. J. A. Berson, *Angew. Chem. Int. Ed.*, 1996, **35**, 2750-2764.
3. F.-G. Klärner, M. Jones and R. M. Magid, *Acc. Chem. Res.*, 2009, **42**, 169-181.
4. K. Asai, A. Fukazawa and S. Yamaguchi, *Angew. Chem. Int. Ed.*, 2017, **56**, 6848-6852.
5. D. J. M. Lyons, R. D. Crocker and T. V. Nguyen, *Chem. Eur. J.*, 2018, **24**, 10959-10965.
6. R. V. Williams, W. D. Edwards, P. Zhang, D. J. Berg and R. H. Mitchell, *J. Am. Chem. Soc.*, 2012, **134**, 16742-16752.
7. G. A. Olah and G. Liang, *J. Org. Chem.*, 1975, **40**, 2108-2116.
8. K. Yamane, H. Yamamoto and M. Nitta, *J. Org. Chem.*, 2002, **67**, 8114-8122.
9. R. Breslow, *J. Am. Chem. Soc.*, 1957, **79**, 5318-5318.
10. R. Breslow, J. T. Groves and G. Ryan, *J. Am. Chem. Soc.*, 1967, **89**, 5048-5048.
11. R. Breslow, *Chem. Rec.*, 2014, **14**, 1174-1182.
12. R. R. Naredla and D. A. Klumpp, *Chem. Rev.*, 2013, **113**, 6905-6948.
13. K. Komatsu and T. Kitagawa, *Chem. Rev.*, 2003, **103**, 1371-1428.
14. R. M. O'Ferrall, in *Adv. Phys. Org. Chem.*, ed. J. P. Richard, Academic Press, 2010, vol. 44, pp. 19-122.
15. J. Bah and J. Franzén, *Chem. Eur. J.*, 2014, **20**, 1066-1072.
16. V. R. Naidu, S. Ni and J. Franzén, *ChemCatChem*, 2015, **7**, 1896-1905.
17. Y. Huang, C. Qiu, Z. Li, W. Feng, H. Gan, J. Liu and K. Guo, *ACS Sustainable Chem. Eng.*, 2016, **4**, 47-52.
18. E. Follet, P. Mayer and G. Berionni, *Chem. Eur. J.*, 2017, **23**, 623-630.
19. P. Pommerening, J. Mohr, J. Friebel and M. Oestreich, *Eur. J. Org. Chem.*, 2017, **16**, 2312-2316.
20. K. Luo, L. Zhang, H. Jiang, L. Chen and S. Zhu, *Chem. Commun.*, 2018, **54**, 1893-1896.
21. K. G. Torma, K. Voronova, B. Sztáray and A. Bodi, *J. Phys. Chem. A*, 2019, **123**, 3454-3463.
22. W. Von E. Doering and L. Knox, *J. Am. Chem. Soc.*, 1957, **79**, 352-356.
23. J. M. Allen and T. H. Lambert, *J. Am. Chem. Soc.*, 2011, **133**, 1260-1262.
24. S.-i. Naya, T. Tokunaka and M. Nitta, *J. Org. Chem.*, 2004, **69**, 4732-4740.
25. B. D. Kelly and T. H. Lambert, *J. Am. Chem. Soc.*, 2009, **131**, 13930-13931.
26. T. Guo, Y. Gao, Z. Li, J. Liu and K. Guo, *Synlett*, 2019, **30**, 329-332.
27. N. R. Panguluri, M. Samarasimhareddy, C. Madhu and V. V. Sureshbabu, *Synlett*, 2014, **25**, 1001-1005.
28. T. Stach, J. Dräger and P. H. Huy, *Org. Lett.*, 2018, **20**, 2980-2983.
29. T. V. Nguyen and A. Bekensir, *Org. Lett.*, 2014, **16**, 1720-1723.
30. T. V. Nguyen and M. Hall, *Tetrahedron Lett.*, 2014, **55**, 6895-6898.
31. T. V. Nguyen and D. J. M. Lyons, *Chem. Commun.*, 2015, **51**, 3131-3134.

32. C. Jandl, D. C. Mayer and A. Pöthig, *Eur. J. Org. Chem.*, 2017, **29**, 4255-4259.
33. M. I. Vinnik and N. G. Zarakhani, *Russ. Chem. Rev.*, 1967, **36**, 51-64.
34. R. M. de Figueiredo, J.-S. Suppo and J.-M. Campagne, *Chem. Rev.*, 2016, **116**, 12029-12122.
35. G. Dahlhoff, J. P. M. Niederer and W. F. Hoelderich, *Cat. Rev.*, 2001, **43**, 381-441.
36. K. Marchildon, *Macromol. React. Eng.*, 2011, **5**, 22-54.
37. M. Hashimoto, Y. Obora, S. Sakaguchi and Y. Ishii, *J. Org. Chem.*, 2008, **73**, 2894-2897.
38. M. Hashimoto, Y. Obora and Y. Ishii, *Org. Process Res. Dev.*, 2009, **13**, 411-414.
39. N. An, B. X. Tian, H. J. Pi, L. A. Eriksson and W. P. Deng, *J. Org. Chem.*, 2013, **78**, 4297-4302.
40. B. X. Tian, N. An, W. P. Deng and L. A. Eriksson, *J. Org. Chem.*, 2013, **78**, 6782-6785.
41. V. Fernández-Stefanuto, P. Verdía and E. Tojo, *New J. Chem.*, 2017, **41**, 12830-12834.
42. Y. Gao, J. Liu, Z. Li, T. Guo, S. Xu, H. Zhu, F. Wei, S. Chen, H. Gebru and K. Guo, *J. Org. Chem.*, 2018, **83**, 2040-2049.
43. K. Hyodo, G. Hasegawa, N. Oishi, K. Kuroda and K. Uchida, *J. Org. Chem.*, 2018, **83**, 13080-13087.
44. X. Mo, T. D. R. Morgan, H. T. Ang and D. G. Hall, *J. Am. Chem. Soc.*, 2018, **140**, 5264-5271.
45. Y. Chen, D. Cantillo and C. O. Kappe, *Eur. J. Org. Chem.*, 2019, **11**, 2163-2171.
46. V. P. Srivastava, R. Patel, Garima and L. D. S. Yadav, *Chem. Commun.*, 2010, **46**, 5808-5810.
47. C. M. Vanos and T. H. Lambert, *Chem. Sci.*, 2010, **1**, 705-708.
48. Y. Furuya, K. Ishihara and H. Yamamoto, *J. Am. Chem. Soc.*, 2005, **127**, 11240-11241.
49. S. Chandrasekhar, in *Comprehensive Organic Synthesis II (Second Edition)*, ed. P. Knochel, Elsevier, Amsterdam, 2014, pp. 770-800.
50. M. Keita, M. Vandamme and J.-F. Paquin, *Synthesis*, 2015, **47**, 3758-3766.
51. L. Yu, H. Li, X. Zhang, J. Ye, J. Liu, Q. Xu and M. Lautens, *Org. Lett.*, 2014, **16**, 1346-1349.
52. X. Zhang, J. Sun, Y. Ding and L. Yu, *Org. Lett.*, 2015, **17**, 5840-5842.
53. R. Ding, Y. Liu, M. Han, W. Jiao, J. Li, H. Tian and B. Sun, *J. Org. Chem.*, 2018, **83**, 12939-12944.
54. R. Ankita and Y. L. D. S., *Eur. J. Org. Chem.*, 2013, **10**, 1889-1893.
55. B. Föhlisch, P. Bürgle and D. Krockenberger, *Chem. Ber.*, 1968, **101**, 2717-2730.
56. C. Jandl and A. Pothig, *Acta Cryst.*, 2017, **73**, 810-813.
57. N. C. Ganguly and P. Mondal, *Synthesis*, 2010, **21**, 3705-3709.
58. R. S. Ramón, J. Bosson, S. Díez-González, N. Marion and S. P. Nolan, *J. Org. Chem.*, 2010, **75**, 1197-1202.
59. L. D. S. Yadav, R. Patel and V. P. Srivastava, *Synthesis*, 2010, **11**, 1771-1776.
60. H. J. Kiely-Collins, I. Sechi, P. E. Brennan and M. G. McLaughlin, *Chem. Commun.*, 2018,

54, 654-657.
61. M. T. Nguyen, G. Raspoet and L. G. Vanquickenborne, *J. Am. Chem. Soc.*, 1997, **119**, 2552-2562.
62. M. Boero, T. Ikeshoji, C. C. Liew, K. Terakura and M. Parrinello, *J. Am. Chem. Soc.*, 2004, **126**, 6280-6286.
63. S. Yamabe, N. Tsuchida and S. Yamazaki, *J. Org. Chem.*, 2005, **70**, 10638-10644.
64. Y. Yamamoto, H. Hasegawa and H. Yamataka, *J. Org. Chem.*, 2011, **76**, 4652-4660.
65. P. Crochet and V. Cadierno, *Chem. Commun.*, 2015, **51**, 2495-2505.
66. Y. Guobing, Z. Yan and W. Jianbo, *Adv. Synth. Catal.*, 2017, **359**, 4068-4105.
67. A. W. Chapman, *J. Chem. Soc.*, 1935, 1223-1229.
68. Note. To validate the proposed intermediate **F** in the self-propagating cycle of the Beckmann rearrangement, imidoyl chloride **H** was syn-thesized (see Scheme S3), H initiated the rearrangement equally ef-fective as that of chlorotropylium chloride.



H