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A facile metal-free one-flask synthesis of multi-substituted furans *via* a $BF_3 \cdot Et_2O$ mediated formal [4 + 1] reaction of 3-chloro-3-phenyldiazirines and α,β-alkenyl ketones†

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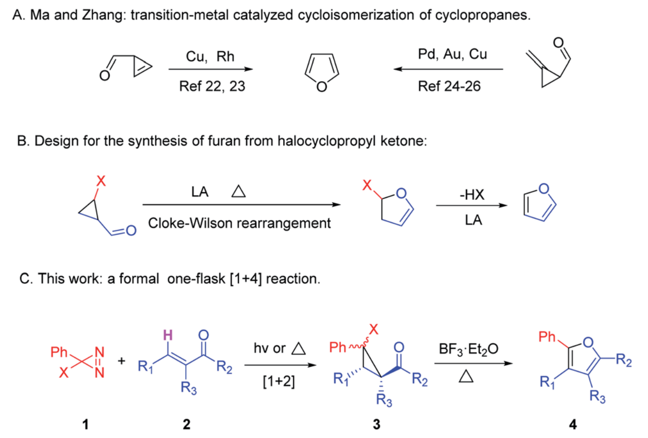
A facile, efficient and metal free one-flask approach to diversely substituted furans from easily accessible 3-chloro-3-phenyldiazirines and α,β-alkenyl ketones is reported. This protocol integrates three steps of cyclopropanation, Cloke–Wilson rearrangement and elimination of HCl in one-flask to give products in moderate to good yields. It provides a metal and oxidant free approach to multi-substituted furans with the advantages of easy operation, mild reaction conditions and a broad scope of substrates.

Introduction

Furan is a five-membered oxygenated heteroaromatic which is widely spread in natural products[1] and plays an important role in both pharmaceutical chemistry[2,3] and in synthetic organic chemistry as a useful building block.[2,4–6] Long attracting the interests of chemists, a number of synthetic methods for furan have been developed,[3,7–12] including the cyclodehydration of dicarbonyl compounds through Paal–Knorr synthesis[13] and Feist–Bénary cyclocondensation.[14,15] Nevertheless, more selective approaches to multi-substituted furans under mild conditions still remain a challenging task.

In the past decades, cyclopropane has been widely used as a three-carbon synthon to access variable chemicals due to the readiness of ring-opening from high angle and torsion strain and tunable reactivity by substituent-controlled C–C bond polarization/cleavage.[16–21] Transition-metal catalyzed intramolecular ring-opening cycloisomerization of cyclopropenyl ketones[22,23] or alkylidene cyclopropyl ketones[24–26] has been proved to be a very successful and reliable approach to furans (Scheme 1A). Early in 2003, Ma and Zhang[22] developed a regioselective cycloisomerization of cyclopropenyl ketones using copper(I) or Pd catalysts. Later in 2004, they developed a Pd mediated ring-opening cycloisomerization of 2-methylene- or alkylidene cyclopropyl ketone to di- or tri-substituted furans.[24] In 2007, Liang group reported a synthesis of trisubstituted furans *via* a Cu(I)-catalyzed formal [4 + 1] cycloaddition of α,β-alkynyl ketones with diazoacetates.[27] Xu and co-workers further developed a Cu–Pd relay catalysis to access tetra-substituted furans from cyclopropenes.[28] These elegant transition-metal catalyzed methods are advantageous in both atom economy and efficiency. However, using alternative non-metal catalysts to promote cycloisomerization is very essential in account of economic, environmental and sustainability requirement. Recently, Wang and coworkers[29–31] have developed I_2/K_2CO_3 or DBU mediated ring opening and cyclization of cyano-substituted cyclopropyl ketones to afford furan derivatives.

The Cloke–Wilson rearrangement (CWR) reaction has been intensively used to access dihydrofurans from cyclopropyl ketones.[32–37] Besides transition-metal catalysis,[38,39] CWR reaction can also be promoted by Lewis acid,[40,41] photocatalysis,[42–44] and organo-catalysis.[26,32,33] Regrettably, an extra dehydrogenation procedure is a prerequisite to transform dihydrofurans to furans using stoichiometric oxidants such as DDQ.[45,46] To avoid



Scheme 1 Synthesis of furan from cyclopropanes by literature and this work.

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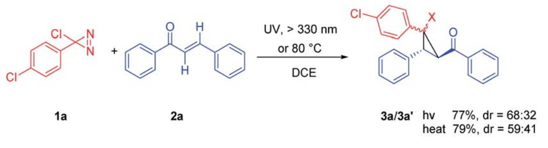
the harmful oxidation procedure, we envisioned that halocyclopropyl ketone is an ideal alternative precursor to perform CWR reaction to deliver halogenated dihydrofuran, which is converted to furan *via* elimination of HX (Scheme 1B). However, there are few reports making use of this elimination strategy. As an elegant example, Namboothiri's group reported that acidic Al_2O_3 could be used to promote CWR reaction of dibromocyclopropyl ketone followed by elimination to access 3-bromo furans.[47,48]

Taking advantage of the fact that the highly reactive halocarbenes (RCX) derived from the easily available 3-halodiazirines (RCN_2X) upon the loss of N_2 readily take part in [2 + 1] cycloaddition with alkenes to give halogenated cyclopropanes,[49–52] we design a formal [4 + 1] approach to furans using this cyclopropanation method to obtain the required halocyclopropyl ketone precursors (Scheme 1C). Firstly, photolysis or thermolysis of 3-halo-3-phenyldiazirine **1** in the presence of α,β-alkenyl ketone **2** gives the halocyclopropyl ketone **3**, which is then subjected to a tandem CWR–elimination reaction sequence to afford the furan **4**. We further succeeded in using the same Lewis acid to promote both the CWR and the elimination reactions to facilitate the reaction procedure. As a result, we herein report a one-flask metal-free synthetic approach to a diversity of di-, tri- or tetra-substituted furans from a series of 3-halo-3-phenyldiazirines and α,β-alkenyl ketones *via* cyclopropanation and $BF_3 \cdot Et_2O$ mediated CWR–elimination reactions.

Results and discussions

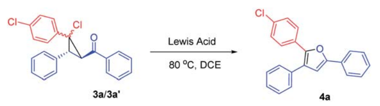
Initially, the synthesis of halocyclopropyl ketones was investigated (Scheme 2). Photolysis or thermolysis of 3-chloro-3-(4-chlorophenyl)diazirine (**1a**) was used to generate phenylchlorocarbene (PhCCl) *in situ*, which rapidly reacted with chalcone (**2a**) to give the halocyclopropyl ketone diastereomers (**3a**/**3a′**). After an optimization of solvents and temperatures (for details, please see Table S1†), either photolysis at room temperature or thermolysis at 80 °C in 1,2-dichloroethane (DCE) gave the halocyclopropyl ketones (**3a**/**3a′**) in highest yield with similar diastereoselectivity.

Next, the transformation of halocyclopropyl ketone **3a** (major isomer) to furan **4a** was investigated and selected results are summarized in Table 1 (for more details, see Table S2†). Lewis acid promoters $FeCl_3 \cdot 6H_2O$, $TiCl_4$ and $FeCl_2 \cdot 4H_2O$ were the most efficient catalysts for this conversion (0.08–0.5 h), while $BF_3 \cdot Et_2O$, $AlCl_3$, $SnCl_4$ and $Sc(OTf)_3$ promoted the reaction less efficiently (15–45 h). Delightfully, furan **4a** was obtained in excellent yields (85–98%) in the presence of these seven catalysts (entries 1–7). On the contrary, $BiCl_3$ couldn't complete this transformation in 72 h and gave **4a** in lower yield (entry 8). No reaction could take place in the absence of a Lewis acid (entry 9). Brønsted acid *para*-toluene sulfonic acid (PTSA) could also mediate this reaction to give **4a** in 90% yield in 36 h (entry 10). Therefore, among these promoters, $BF_3 \cdot Et_2O$ and $FeCl_2 \cdot 4H_2O$ showed the best catalytic activity to give nearly quantitative yields of **4a**. It is also noted that the halocyclopropyl ketone diastereomer **3a′** was similarly converted to **4a** in the nearly quantitative yield as **3a** in the presence of either $BF_3 \cdot Et_2O$ or $FeCl_2 \cdot 4H_2O$ (entries 12–13). Therefore, there is no need to separate two diastereomers **3a**/**3a′** for the transformation to **4a**. We then succeeded in implementing these reaction steps in one-flask (for details, please see Table S3†) with $BF_3 \cdot Et_2O$ (1 eq.) as the best catalyst, which was added into the flask after the completion of cyclopropanation to avoid side reactions. This one-flask protocol gave **4a** in an overall yield of 68%.



Scheme 2 Synthesis of halo-cyclopropyl ketone **3a**/**3a′**.

Table 1 Screening of Lewis acids for **4a**[a]



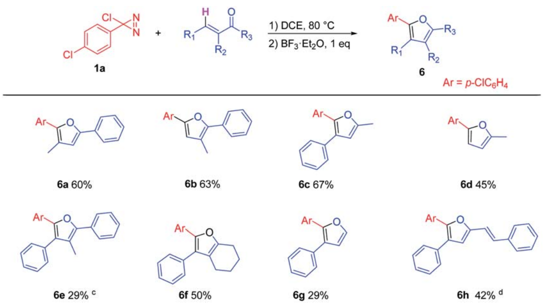
Entry	Lewis acid	Time, h	Yield,[b] %
1	$TiCl_4$	0.16	86
2	$FeCl_2 \cdot 4H_2O$	0.5	96
3	$FeCl_3 \cdot 6H_2O$	0.08	86
4	$BF_3 \cdot Et_2O$	15	98
5	$AlCl_3$	17	90
6	$SnCl_4$	21	87
7	$Sc(OTf)_3$	45	86
8	$BiCl_3$	72	68[c]
9	None	24	NR
10	PTSA	36	90
11[d]	$FeCl_2 \cdot 4H_2O$	1	97
12[e]	$BF_3 \cdot Et_2O$	16	98
13[d,e]	$FeCl_2 \cdot 4H_2O$	1	97

[a] Reagents and conditions: halocyclopropyl ketone **3a** (0.06 mmol), Lewis acid (0.06 mmol, 1 eq.) in 5 mL DCE was heated at 80 °C in a 38 mL reaction tube equipped with a condenser until the reaction was completed by TLC monitoring. NR = no reaction. RSM = recovery of starting material. [b] Isolated yield. [c] Yield is based on consumed halocyclopropyl ketone. RSM was 16%. [d] 0.2 eq. LA was used. [e] **3a′** was used instead of **3a**.

With this optimized one-flask conditions in hand, we investigated the scope of *para*-substituted phenylchlorodiazirines **1** (Table 2). Unsubstituted (R = H) or substituted phenylchlorodiazirines with either electron-donating (R = Me, OMe) or slightly electron withdrawing (R = F, Cl) groups on the phenyl ring gave furans (**4a–4e**) in good yields (57–71%). However, the cyclopropyl ketones with strong electron-withdrawing substituents such as CF_3 or CN (**3f**, **3g**) need to be heated in *n*-octane at 120 °C to give furans in reasonable yields (**4f** 43%; **4g** 42%) due to lower ring opening reactivity for less polarization character of C–C bond. This conversion could also be driven by the powerful $FeCl_3 \cdot 6H_2O$ and gave furans in better yields (**4f** 57%; **4g** 53%). However, the reaction of 3-benzyl-3-chloro-diazirine ($PhCH_2CClN_2$) and chalcone couldn't afford the expected furan. The scope of chalcones were also investigated: chalcones with substituents on either phenyl ring gave furans (**5a–5i; 5m–5t**) in good yields (70–80%), no matter they are electron-withdrawing or electron-donating. This one-flask strategy can also be applied to the naphthyl, thiophenyl or pyridinyl substituted chalcones to afford furans (**5j–5l, 5u**) with moderate to good yields (40–78%).

We further extended this one-flask reaction to a wide range of alkenyl ketones with alkyl groups, and the corresponding furans were obtained in moderate to good yields (Table 3). Alkenyl ketones substituted with a methyl group at R_1, R_2 or R_3 position gave trisubstituted furans **6a–6c** in good yields (60–67%). Methyl vinyl ketone (MVK) gave 2-methyl-5-phenyl furan **6d** in 45% yield. Notably, this protocol enabled an astonishing access to tetra-substituted furans with structural complexity (**6e**, **6f**). For example, 2-benzylidenecyclohexan-1-one gave tetra-substituted furan **6f** with a fused ring in good yield (50%). This protocol can also be applied to α,β-unsaturated aldehydes, *e.g.*, cinnamaldehyde was used to synthesize 2,3-disubstituted furan **6g** in 29% yield. Bis(2-phenylvinyl) ketone gave furan **6h** in 42% yield, exemplifying the functional group tolerance for another sensitive C═C double bond. Step-by-step analysis of these two-stage reactions (Table S5†) reveals that the lower yields were owing to the poor cyclopropanation reactivity because of less electronic richness (**6d**, **6g**) or steric hindrance (**6e**) of the C═C double bond, in which a considerable amount of carbene dimer was often generated as side product. Therefore, this one-flask protocol can use a variety of α,β-unsaturated carbonyl substrates to synthesize 2,3- or 2,5-disubstituted, 2,3,5-trisubstituted and even 2,3,4,5-tetrasubstituted furans with moderate to good yields.

Table 3 Scope of alkyl substituted alkenyl ketones[a,b]

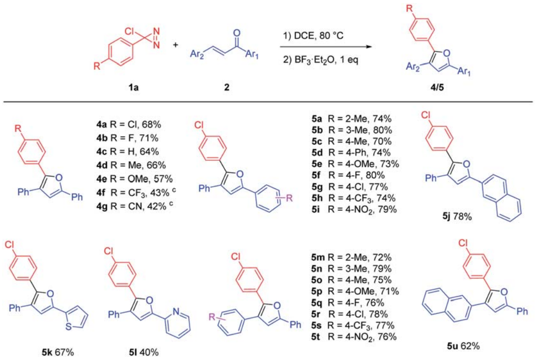


[a] Reagents and conditions: using method A as above unless specified. [b] Isolated yield of one-flask reaction. [c] **1a** (0.2 mmol) was reacted with 2 eq. alkenyl ketone (0.4 mmol). [d] Two equivalents of alkenyl ketone were used and reactions were performed at 60 °C in both stages.

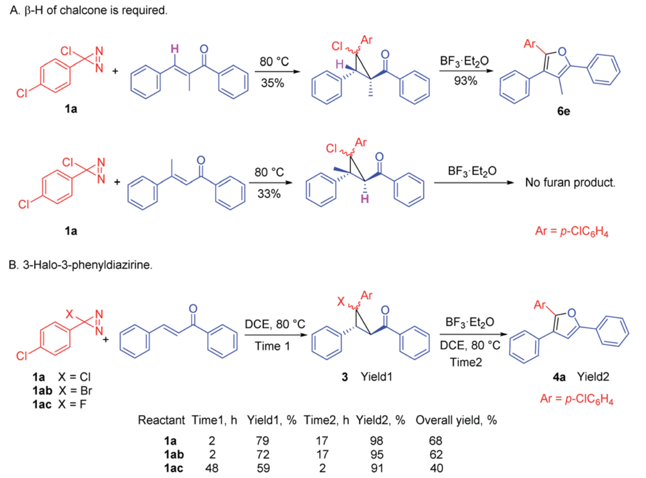
To probe the mechanism of these reactions, β-methyl chalcone was subjected to this one-flask reaction (Scheme 3A). Unlike the α-methyl chalcone, the CWR–elimination reaction of the cyclopropyl ketone promoted by BF_3 gave a complicated mixture without any furan product, indicating the necessity of a β-hydrogen. Reactivities of other 3-halo-3-phenyldiazirines (X = Br, F) were also studied (Scheme 3B). 3-Bromo-3-phenyldiazirine (**1ab**) gave bromocyclopropyl ketone **3ab**/**3ab**′ in 2 h (72%), which gave furan **4a** in 95% yield in 17 h with similar reactivity as **3a**/**3a**′ (X = Cl). It indicates that BF_3 is supposed to bind with the oxygen in carbonyl group instead of halogen to promote the CWR reaction, leading to no significant difference in the reactivities between **3a** and **3ab** (Scheme 4, path a). On the other hand, 3-fluoro-3-phenyldiazirine (**1ac**) gave the cyclopropyl ketone **3ac** (59%) much slower (48 h) owing to the less electrophilicity and stability of phenylfluorocarbene (PhCF).[53,54] Moreover, **3ac** is quite ready to give furan **4a** in 90% yield with excellent reactivity (2 h). This efficient transformation is supposed to be attributed to a different pathway because of the high affinity between BF_3 and fluorine (*vide infra*).

Based on these experiments and literature,[34,47,55] a plausible mechanism is proposed in Scheme 4. Upon thermolysis or photolysis, 3-halo-3-phenyldiazirine (**1**) generates electrophilic singlet phenylhalocarbene (PhCX) with the loss of nitrogen

Table 2 Scope of substrates[a,b]

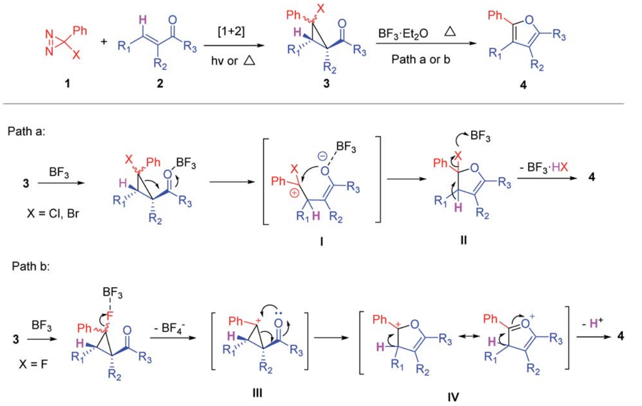


[a] Reagents and conditions (method A): 3-aryl-3-chlorodiazirine **1** (0.2 mmol), alkenyl ketone **2** (0.2 mmol) in 5 mL DCE was heated at 80 °C in a 38 mL reaction tube with a condenser until the reaction was completed (usually 2 h). $BF_3·Et_2O$ (0.2 mmol, 1 eq.) was added in and kept on heating to complete the transformation. [b] Isolated yield of one-flask reaction. [c] Reacted at 120 °C in *n*-octane and $BF_3·Et_2O$ (5 eq.) was used.



Reactant	Time1, h	Yield1, %	Time2, h	Yield2, %	Overall yield, %
1a	2	79	17	98	68
1ab	2	72	17	95	62
1ac	48	59	2	91	40

Scheme 3 Control experiments.



Scheme 4 Plausible mechanism.

(N_2).[51,56] The PhCX carbene reacts rapidly with α,β-alkenyl ketone (**2**) to afford halocyclopropyl ketone (**3**) *via* a [2 + 1] cycloaddition. Subsequent addition of $BF_3 \cdot Et_2O$ catalyzes the CWR rearrangement of chloro- or bromocyclopropyl ketone **3a**/**3ab** by complexing with the carbonyl oxygen in **3** (path a) to facilitate the heterolytic cleavage of this donor–acceptor cyclopropane to give the key zwitterion intermediate **I**. Then, an intramolecular cyclization of **I** by nucleophilic attack of oxy-anion to carbocation gives dihydrofuran **II**, which is converted to furan **4** after the loss of HX with the aid of BF_3. In the case of fluorocyclopropyl ketone **3ac**, the ring-opening might be driven by the loss of tetrafluoroborate (BF_4^-) and proceeds through a cyclopropyl carbocation mechanism in a similar intramolecular cyclization mode (path b).

Conclusions

In conclusion, we have developed a facile one-flask approach to the di-, tri- and even tetra-substituted furans in moderate to good yields from readily available starting materials using inexpensive boron trifluoride as catalyst. This metal and oxidant free method involves the cyclopropanation of α,β-alkenyl ketones with phenylchlorocarbene, BF_3 mediated ring-opening cycloisomerization (Cloke–Wilson rearrangement) and elimination of HCl to give the multi-substituted furans. This method has the advantages of simple operation, mild reaction conditions and a broad scope of substrates, which provides a concise approach to diversified biologically and synthetically useful furans. We believe it will benefit the discovery of new application of furan derivatives.

Author contributions

Z. Zhang: most of the experimental work and writing of ESI.† A. Huang & L. Ma: methodology and discussion. J. Xu: manuscript revision and discussion. M. Zhang: conceptualization, funding acquisition, supervision, and writing, review, and editing of the manuscript.

Conflicts of interest

The authors declare no competing financial interest.

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