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An Efficient Iron-Catalyzed Carbon–Carbon Single-Bond Cleavage via Retro-Claisen Condensation: A Mild and Convenient Approach to Synthesize a Variety of Esters or Ketones

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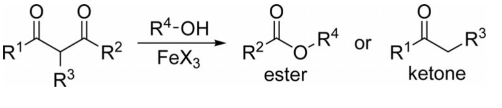
An efficient iron-salt-catalyzed carbon–carbon bond cleavage occurring through a retro-Claisen condensation reaction has been developed. The reaction is useful for the synthesis of a variety of esters or ketones under mild conditions. This method works under solvent-free conditions without the need of an inert atmosphere. This protocol is also applicable for the one-pot syntheses of ketones through tandem carbon–carbon bond formation (substitution or Michael) followed by a retro-Claisen reaction. However, for Michael adducts, ring annulation takes place subsequently. Notably, this method is very simple, convenient, high yielding, and only a catalytic (5 to 10 mol-%) amount of $Fe(OTf)_3$ is needed.

Introduction

Transition-metal-catalyzed reactions are among the most powerful tools in modern organic synthesis. Extensive research has been done in the development of palladium-, ruthenium-, rhodium-, iridium-, and even nickel-catalyzed reactions. However, due to the high cost and toxic nature of many of these metal catalysts, there has been a recent surge in the development of organic transformations catalyzed by much cheaper and more environmentally friendly metals. In this regard, iron has received a great deal of attention as an effective and promising alternative transition metal in the field of catalysis due to its high abundance, low price, and environmentally friendly characteristics.[1] As a consequence, a series of novel iron-catalyzed organic transformations have been developed. Since the pioneering research work of Tamura and Kochi,[2] a number of reactions including iron-catalyzed oxidation,[3] hydrogenation,[4] hydrosilylation,[5] rearrangement,[6] Michael addition,[7] carbon–carbon[8–10] and carbon–heteroatom bond-forming reactions,[11] and oxidative coupling of arynes[12] have been extensively studied. In addition to that, various iron-catalyzed cross-coupling reactions including Sonogashira,[13] Heck,[14] Kumada,[15] Negishi,[16] and Suzuki[17] reactions have also been developed. Moreover, iron salts have been successfully employed for the synthesis of various heterocyclic compounds by us and other groups.[18] More recently, we[19] and others[20] have also discovered novel iron-catalyzed activation of alcohols towards various nucleophiles. Therefore, considering these advantages and the diversity of iron, the discovery of new iron-catalyzed reactions and methodologies is still very much in demand in both academia and industrial research.

On the other hand, the catalytic cleavage of a carbon–carbon single bond by transition-metal complexes is a potentially useful organic transformation, for which, extensive studies have been done.[21] However, in most of the reactions, highly strained compounds such as three- or four-membered carbocycles[22] and compounds with good leaving groups[23] or chelating compounds[24] have been demonstrated as substrates. Therefore, the development of new reactions and reagents for the catalytic cleavage of the carbon–carbon bond remains a challenging issue.

During our recent investigation of iron-salt-mediated direct alkylation of active methylene compounds with benzylic and allylic alcohols,[19d] we noticed that when an aliphatic alcohol was treated with acetylacetone, an ester was produced by direct carbon–carbon bond cleavage through a retro-Claisen condensation type reaction.[25] This observation encouraged us to study systematically the scope of this reaction in organic synthesis. Herein, we wish to report our discovery of an efficient, mild, and inexpensive iron(III) trifluoromethanesulfonate mediated carbon–carbon bond cleavage reaction for the synthesis of esters or ketones from acetylacetone and their derivatives by direct



Scheme 1. Iron-salt-catalyzed retro-Claisen condensation reaction.

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carbon–carbon bond cleavage through a retro-Claisen condensation reaction without the use of traditional organic solvents (Scheme 1).

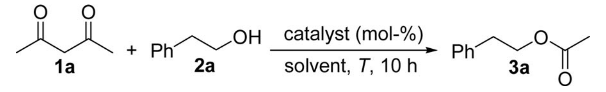
Results and Discussion

Synthesis of Esters

Ester formation is a fundamental reaction in organic synthesis, as esters are very important in daily life and in various fields of organic synthesis. Consequently, various methods have been developed,[26] and still it is highly desirable to develop a new and cost-saving reaction for the preparation of esters under neutral mild conditions. The reaction we wish to report here for the synthesis of esters is general, convenient, and less expensive, and it works under neutral conditions without any solvents in the presence of catalytic iron salt.

To optimize the reaction conditions, we initially studied the reaction between phenethyl alcohol (**2a**) and acetylacetone (**1a**) in different solvents, at different temperatures, and with different amounts of the catalyst (Table 1). No reaction took place in 1,2-dichloroethane at 80 °C in the presence of 10 mol-% of FeCl$_3$ (Table 1, Entry 1); 78% yield of the desired product was obtained when the reaction was carried out under neat conditions (Table 1, Entry 2). The product was obtained in almost the same yield with the use of 5 mol-% of FeCl$_3$ (Table 1, Entry 3). Upon reduction of the amount of catalyst to 3 mol-%, the yield of the product decreased (Table 1, Entry 4). Next, we examined different iron salts (5 mol-%) at 80 °C without using any solvents to study their catalytic activities towards this reaction. FeBr$_3$ also catalyzed the reaction and afforded the desired product in 72% yield (Table 1, Entry 5), whereas no reaction took place in the presence of Fe(acac)$_3$ (Table 1, Entry 9). It was observed that the reaction proceeded more efficiently when Fe(OTf)$_3$ (5 mol-%) was used as the catalyst to produce the product in almost quantitative yield (Table 1, Entry 6). Decreasing the temperature as well as the amount of Fe(OTf)$_3$ led to a decrease in the yield of the desired product (Table 1, Entries 7 and 8). The efficiency of Fe(OTf)$_3$ can be explained from the fact that metal triflates are more stable in protic media such as water and alcohols; moreover, iron(III) triflate is a stronger Lewis acid than FeCl$_3$. The Brønsted acids TfOH and HCl were tested to catalyze this reaction; however, the desired products were obtained in very low yield even when the reaction was heated for a long period of time (Table 1, Entries 10 and 11). From this observation it may be concluded that the iron salt is directly involved in the catalytic process. However, the generation and involvement of partly formed Brønsted acid cannot be completely over ruled in this transformation. The reaction did not proceed without any catalyst.

Table 1. Reactions of acetylacetone (**1a**) with phenethyl alcohol (**2a**) under various conditions in the presence of different catalysts.[a]

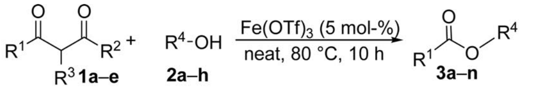


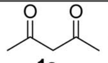
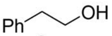
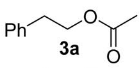
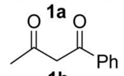
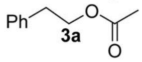
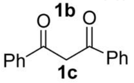
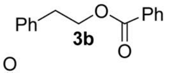
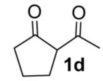
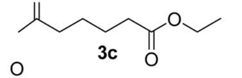
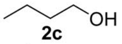
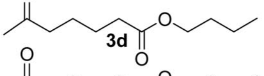
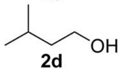
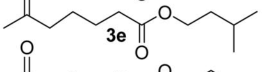
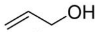
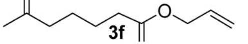
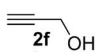
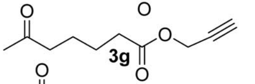
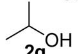
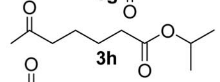
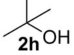
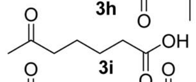
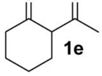
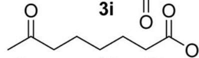
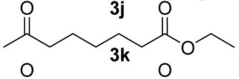
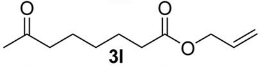
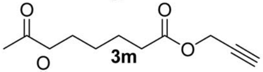
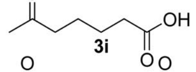
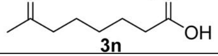
Entry	Catalyst (mol-%)	Solvent	T [°C]	Yield [%][b]
1	FeCl$_3$ (10)	1,2 DCE[c]	80	N.R.[d]
2	FeCl$_3$ (10)	no solvent	80	78
3	FeCl$_3$ (5)	no solvent	80	79
4	FeCl$_3$ (3)	no solvent	80	70
5	FeBr$_3$ (5)	no solvent	80	72
6	Fe(OTf)$_3$[e] (5)	no solvent	80	98
7	Fe(OTf)$_3$ (3)	no solvent	80	92
8	Fe(OTf)$_3$ (5)	no solvent	60	22
9	Fe(acac)$_3$[f] (5)	no solvent	80	N.R.[d]
10	TfOH (15)	no solvent	80	36
11	HCl (15)	no solvent	80	27

[a] Reaction conditions: **1a** (1 mmol), **2a** (1 mmol), and catalyst (0.05 mmol). [b] Pure, isolated yield after column chromatography. [c] 1,2-DCE = 1,2-dichloroethane. [d] N.R. = no reaction. [e] Fe(OTf)$_3$ = iron(III) trifluoromethanesulfonate. [f] Fe(acac)$_3$ = iron(III) acetylacetonate.

After optimizing the reaction conditions, we used different types of 1,3-diketones as well as alcohols; the results are summarized in Table 2. Alcohol **2a** was found to react efficiently with unsymmetrical 1,3-diketone such as acetylacetophenone (**1b**) chemoselectively, producing ester **3a** in 85% yield (Table 2, Entry 2); that is, the alcohol attacked only at the more reactive carbonyl carbon atom. Likewise, benzoylacetophenone (**1c**) also reacted with phenethyl alcohol (**2a**) to give benzoyl ester **3c** (Table 2, Entries 2 and 3). However, due to the low reactivity of the carbonyl carbon atom of compound **1c** the reaction worked at higher temperature (120 °C); under these conditions, desired product **3c** was obtained in 87% yield. Moreover, cyclic 1,3-diketones such as 2-acetylcyclopentanone (**1d**) and 2-acetylcyclohexanone (**1e)** also underwent smooth carbon–carbon bond cleavage with various alcohols in a highly regiospecific manner to yield exclusively the corresponding acyclic keto esters (Table 2, Entries 4–9, 11–14) in high yields. Simple aliphatic alcohols such as methanol (**2i**), ethanol (**2b**), *n*-butanol (**2c**), and 3-methylbutanol (**2d**) were found to be equally efficient nucleophiles. Furthermore, allyl (**2e**) and propargyl alcohols (**2f**) also reacted smoothly with **1d** or **1e** to produce the corresponding long-chain keto esters without disturbing the double and triple bonds (Table 2, Entries 7, 8, 13, and 14). The secondary alcohol 2-propanol (**2g**) also reacted with **1d** to produce corresponding keto ester **3h** in 82% yield (Table 2, Entry 9), whereas *tert*-butyl alcohol did not produce the desired ester with the reaction of 2-acetylcyclopentanone (**1d**). Instead, carboxylic acid **3i** was produced (Table 2, Entry 10).[27] However, due to their low boiling points and volatility, all the alcohols except **2a** were used in excess amounts (5 equiv.) with respect to the diketones for their complete conversion to the desired product. It is noteworthy that water also participated in this reaction as a nucleophile, as the reaction of water with cyclic 1,3-diketones **1d** and **1e** produced the corresponding long-chain keto acids in 78 and 87% yield, respectively (Table 2, Entries 15 and 16).

Table 2. Reactions of various 1,3-diketones with various alcohols or water to produce esters or acids.[a]



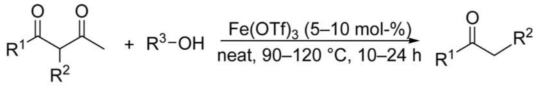
Entry	1,3-Diketone	Alcohol	Product	Yield [%][b]
1	 **1a**	 **2a**	 **3a**	98[c]
2	 **1b**	**2a**	 **3a**	85[c]
3	 **1c**	**2a**	 **3b**	87[c,d]
4	 **1d**	EtOH **2b**	 **3c**	86
5	**1d**	 **2c**	 **3d**	90
6	**1d**	 **2d**	 **3e**	83
7	**1d**	 **2e**	 **3f**	88
8	**1d**	 **2f**	 **3g**	86
9	**1d**	 **2g**	 **3h**	82
10	**1d**	 **2h**	 **3i**	58
11	 **1e**	MeOH **2i**	 **3j**	80
12	**1e**	**2b**	 **3k**	82
13	**1e**	**2e**	 **3l**	75
14	**1e**	**2f**	 **3m**	80
15	**1d**	H_2O **2j**	 **3i**	78
16	**1e**	**2j**	 **3n**	87

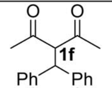
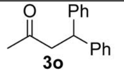
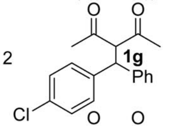
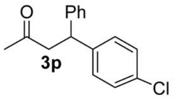
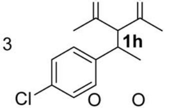
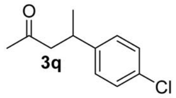
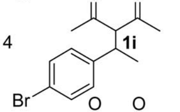
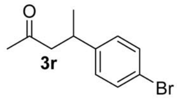
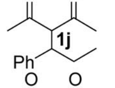
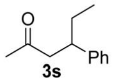
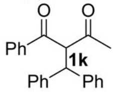
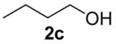
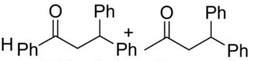
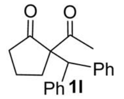
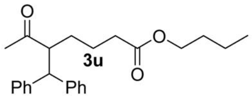
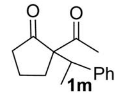
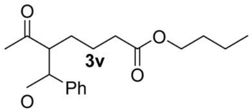
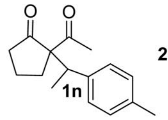
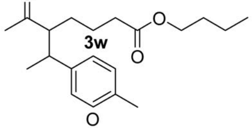
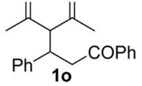
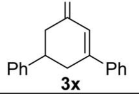
[a] Reaction conditions: 1,3-Diketone (1 mmol), alcohol or water (5 mmol), $Fe(OTf)_3$ (0.05 mmol), neat, 80 °C, 10 h. [b] Pure, isolated yield after column chromatography. [c] 1 mmol of alcohol was used. [d] Reaction was carried out at 120 °C.

Synthesis of Ketones

The derivatives of methyl ketone are important building block in organic synthesis. Moreover, many methyl ketone derivatives are present in flavor and aroma substances, and some methyl ketones are natural products that are generated from decarboxylation of the corresponding fatty acids. Consequently, a wide number of methods have been developed.[28] However, many of these methods suffer from a number of drawbacks such as the use of expensive and toxic chemicals, unavailability of substrates, and cumbersome procedures for product isolation. Therefore, the development of new methods for the synthesis of methyl ketones in terms of efficiency, mild reaction conditions, and operational simplicity in the presence of less-expensive catalysts is still highly desirable. After successful development of a procedure for the synthesis of esters, we applied this retro-Claisen condensation strategy to the synthesis of various methyl ketones. In this strategy, simple aliphatic alcohols such as methanol or butanol were used to cleave the carbon–carbon bond of substituted 1,3-diketones in the presence of a catalytic amount of $Fe(OTf)_3$ so that volatile ester components would be formed and could be removed during workup. The results are summarized in Table 3. A wide range of acetylacetone derivatives underwent the reaction

Table 3. Reactions of various substituted 1,3 diketones with alcohols to produce methyl ketones.[a]



Entry	Diketone	Alcohol	Product	Yield [%][b]
1	 **1f**	MeOH **2i**	 **3o**	85
2	 **1g**	**2i**	 **3p**	83
3	 **1h**	**2i**	 **3q**	70
4	 **1i**	**2i**	 **3r**	68
5	 **1j**	**2i**	 **3s**	76
6	 **1k**	 **2c**	 **3t** (major) **3o** (minor)	45 (**3t**)[c] 25 (**3o**)[c]
7	 **1l**	**2c**	 **3u**	67[d]
8	 **1m**	**2c**	 **3v**	65[d]
9	 **1n**	**2c**	 **3w**	70[d]
10	 **1o**	**2i**	 **3x**	78[e]

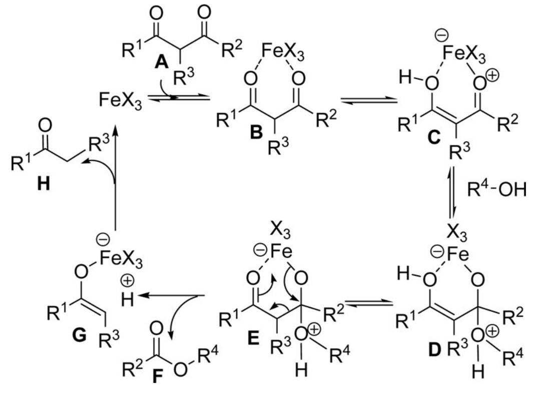
[a] Reaction conditions: 1,3-Diketone (0.5 mmol), alcohol (2.5 mmol), $Fe(OTf)_3$ (0.025 mmol), neat, 90 °C, 12 h; then, $Fe(OTf)_3$ (0.025 mmol), 12 h. [b] Pure, isolated yield after column chromatography. [c] Reaction was carried out at 120 °C. [d] 1,3-Diketone (0.5 mmol), alcohol (2.5 mmol), $Fe(OTf)_3$ (0.025 mmol), neat, 120 °C, 10 h. [e] 1,3-Diketone (0.5 mmol), alcohol (2.5 mmol), $Fe(OTf)_3$ (0.025 mmol), neat, 90 °C, 10 h.

smoothly with methanol (Table 3, Entries 1–5) to afford the desired methyl ketone derivatives in high yields, and in this reaction, volatile methyl acetate was formed as a byproduct. When ethanol was used in place of methanol at 90 °C, a lower yield of the desired product was observed. Probably, at this temperature methanol is a better nucleophile compared to its higher homolog due to steric reason. However, with high boiling alcohols such as *n*-butanol the reaction works efficiently at 120 °C, but the reaction was very slow at 90 °C. So, the size of the alcohol and the effect of temperature are very important for the efficient synthesis of ketones. 1,3-Diketone **1k** (Table 3, Entry 6) reacted efficiently with *n*-butanol to give a mixture of two unequal amounts of ketones at 120 °C; the major product was obtained by the reaction of the alcohol at the more reactive carbonyl carbon atom. Similarly, with substituted cyclic 1,3-diketones such as **1l**, **1m**, and **1n** (Table 3, Entries 7–9), the alcohol reacted chemoselectively at the ring carbonyl carbon atom and produced substituted methyl ketones in good yields. Interestingly, the Michael adduct of acetylacetone **1o** (Table 3, Entry 10) also underwent smooth retro-Claisen condensation; however, under the reaction conditions ring annulations of the intermediate product in the presence of the iron salt took place, leading to cyclohexenone derivative **3x** in 78% yield.

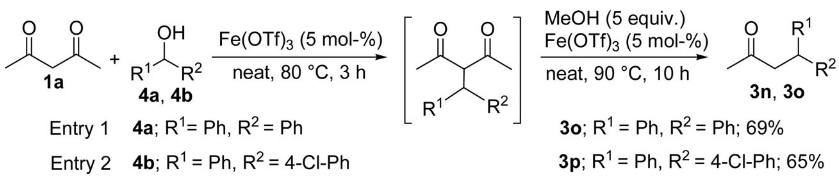
One-Pot Tandem C–C Bond Formations/Retro-Claisen Condensations

To make this protocol more attractive, we investigated the iron-salt-catalyzed tandem carbon–carbon bond formation through direct substitution of benzylic alcohols with acetylacetone[19d] followed by carbon–carbon bond cleavage to achieve ketones in one pot. To our delight, this one-pot reaction also worked efficiently and gave desired products **3o** and **3p** in good yields: 69 and 65%, respectively (Scheme 2). Similarly, we also demonstrated the iron-salt-catalyzed tandem carbon–carbon bond formation through Michael reaction of acetylacetone with α,β-unsaturated ketones[7c] followed by retro-Claisen condensation and ring annulations, leading to the one-pot synthesis of cyclohexenone derivatives **3x** and **3y** in good yields (Scheme 3).

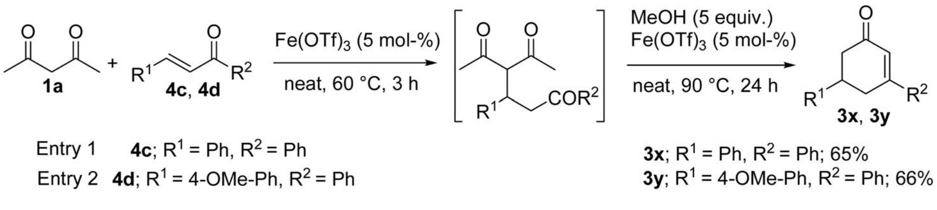
On the basis of the experimental results, a possible mechanism for the iron-salt-catalyzed retro-Claisen condensation of 1,3-diketones is shown in Scheme 4. It is well known that iron salts can coordinate to 1,3-diketones[7c] to thus produce either **B** or **C**. This complexation increases the nucleophilicity at the methylene carbon atom, so it can react with a suitable electrophile such as a benzylic or allylic carbocation, which can be generated from benzyl or allyl alcohol.[19d] Moreover, it also simultaneously increases the electrophilicity of the carbonyl carbon atom, so it can react with suitable nucleophiles such as alcohols and water. Nucleophilic addition of an alcohol affords intermediate **D** or **E**, which then undergoes carbon–carbon bond cleavage through a retro-Claisen condensation reaction and elimination of ester **F** and iron enolate **G**, which after protonation regenerates the catalyst to produce ketone **H**. Depending on the nature of the alcohol or 1,3-diketone it would be possible to synthesize either esters or ketones, as the other component will be volatile and can be separated during isolation of the product.



Scheme 4. A possible mechanism for the iron-catalyzed carbon–carbon bond cleavage reaction.



Scheme 2. Fe(OTf)$_3$-catalyzed tandem C–C bond formation and C–C bond cleavage.



Scheme 3. Fe(OTf)$_3$-catalyzed tandem C–C bond formation, C–C bond cleavage, and ring annulation.

Conclusions

In summary, we have demonstrated a novel and efficient iron-salt-catalyzed carbon–carbon bond cleavage[29] of 1,3-diektones, which occurs through a retro-Claisen condensation reaction. This protocol provides a simple and convenient strategy for the efficient synthesis of structurally diverse esters or substituted methyl ketones. Moreover, tandem carbon–carbon bond formation (through substitution or Michael addition) followed by carbon–carbon bond cleavage in one pot has also been demonstrated. Notably, the use of less expensive and environmentally friendly iron salts makes this protocol very attractive, and it can be useful for large-scale applications.

Experimental Section

Representative Experimental Procedure for the Synthesis of Phenethyl Acetate (3a): A 5-mL screw-cap vial was charged with acetylacetone (100 mg, 1.0 mmol) and phenethyl alcohol (122 mg, 1.0 mmol). To this mixture was added Fe(OTf)$_3$ (25 mg, 0.05 mmol), and the reaction mixture was stirred vigorously with a small magnet at 80 °C for 10 h, keeping the cap of the vial tightly closed. The progress of the reaction was followed by TLC. The reaction mixture was allowed to attain room temperature and was then taken up in ethyl acetate (50 mL). This mixture was washed with water (20 mL) followed by brine solution (20 mL), and the organic phase was dried with anhydrous Na$_2$SO$_4$. The solvent was removed under reduced pressure, and the product was purified by silica gel column chromatography (5% ethyl acetate in petroleum spirit) to afford **3a** (161 mg, 0.98 mmol, 98%) as a yellowish liquid. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.04 (s, 3 H), 2.94 (t, J = 7.1 Hz, 2 H), 4.29 (t, J = 7.1 Hz, 2 H), 7.21–7.34 (m, 5 H) ppm.

Supporting Information (see footnote on the first page of this article): Experimental details and spectroscopic data of all compounds.

Acknowledgments

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