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Iron Chloride Hexahydrate-catalyzed Friedel-Crafts Akylation of Cyclic Ketene Dithioacetals with Alcohols

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Abstract A cost-effective and environmentally compliance $FeCl_3·6H_2O$ catalyzed Friedel-Crafts alkylation of cyclic ketene dithioacetals with alcohols was developed. The reaction was efficient in the presence of catalyst loading as low as 5%(molar fraction) in CH_2Cl_2 solvent at room temperature or under reflux conditions. A wide range of alkylated ketene dithioacetals were synthesized in excellent yields.

Keywords Iron(III) chloride; Olefin; Ketene dithioacetal; Alcohol; Friedel-Crafts alkylation

1 Introduction

The Friedel-Crafts alkylation is one of the prominent methods for the formation of C—C bonds[1—5]. Likewise, alcohols are familiar as green alkylating reagents to establish an environmentally compliance alkylation process with water as sole byproduct[6]. Hence, the Friedel-Crafts alkylation with alcohols has attained considerable attention and has been well documented in recent years[7—9]. Nevertheless, such Friedel-Crafts alkylations are limited to alkylation of arenes and heteroarenes. The reports on the alkylation of olefins with alcohols are rare, owing to the lower nucleophilicity. Ketene dithioacetals are versatile and significant reagents in organic synthesis[10—26] and are considered as polarized internal olefins with highly nucleophilic carbon atom adjacent to the electron-withdrawing group (EWG). The high nucleophilicity is due to the push-pull effect of the alkylthio group and the EWG at either side of the double bond. The high nucleophilic nature of ketene dithioacetals grabbed the attention for the alkylations with alcohols and a few reports have appeared recently[27—29]. For instance, Zhang and co-workers[27] successfully performed alkylation of ketene dithioacetals with various alcohols under $BF_3·OEt_2$-mediated reaction conditions. Later, Wang *et al*.[28] reported $CuBr_2$(30%, molar fraction)-catalyzed alkylation of ketene dithioacetals with benzylic alcohols. Immediately after this report, Song *et al*.[29] realized $FeBr_3$(30%, molar fraction)-catalyzed Friedel-Crafts alkylation between ketene dithioacetals and propargyl alcohols. However, all the above reports suffer from one or more limitations, including the use of expensive metal salts in considerably large quantities and moisture sensitive conditions, which limit their practical utility in organic synthesis. Therefore, the development of a practically more convenient, cost-effective and eco-friendly catalytic method is highly desirable.

$FeCl_3$ is a promising environmentally benign catalyst for a wide range of organic transformations owing to its nontoxic, inexpensive, air and moisture stable and easy to handle nature[30—33]. As the continuation to our research investigations like $FeCl_3$-mediated desulfitative carbon-carbon bond formation between α-oxo ketene dithioacetals and indoles[34] and $FeCl_3$-catalyzed Friedel-Crafts alkylation of indoles with α-hydroxy ketene dithioacetals[35], we here report $FeCl_3·6H_2O$ catalyzed Friedel-Crafts alkylation of cyclic ketene dithioacetals with alcohols.

2 Experimental

All the reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. The products were purified by column chromatography over silica gel(300—400 mesh). All the reactions were monitored by thin layer chromatography(TLC), which was performed on precoated aluminum sheets of silica gel 60(F254). ^1H and ^{13}C NMR spectra were recorded at ambient temperature with a Brucker 400 MHz or a Bruker 100 MHz spectrometer, respectively, using tetramethylsilane(TMS) as internal standard. High resolution mass spectral(HRMS) analysis was achieved on an AB-SCIEX triple TOF 4600 by electron spray ion(ESI) method. All the melting points were uncorrected.

In a typical experiment, to a stirred solution of compounds **1**(0.5 mmol) and **2**(0.75 mmol) in CH_2Cl_2(1 mL) in a round-bottom flask was added $FeCl_3·6H_2O$(0.025 mmol) and the resultant mixture was stirred at room temperature(A) or in reflux(B) until compound **1** was completely consumed. Then 20 mL of water was added and the mixture was extracted with

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CH_2Cl_2(15 mL×3). The combined organic phase was dried over anhydrous $MgSO_4$, and all the volatiles was evaporated under reduced pressure. Purification of the resulting residue by flash silica gel column chromatography[petroleum ether(60—90 °C)/diethyl ether=2:1, volume ratio] afforded products **3** in excellent yields.

The spectroscopic features of the known compounds **3**a[27], **3**f[27], **3**h[27], **3**i[27], **3**p[27], **3**s[27], **3**t[27], **3**v[27] and **3**w[29] are in good agreement with those reported in the literatures.

3-(1,3-Dithiolan-2-ylidene)-4-phenyl-4-*p*-tolylbutan-2-one(**3**b): a white solid; m. p. 123—124 °C. ^{1}H NMR($CDCl_3$, 400 MHz), *δ*: 1.85(s, 3H), 2.34(s, 3H), 3.23—3.28(m, 4H), 5.81(s, 1H), 7.07(d, *J*=8.1 Hz, 2H), 7.12(d, *J*=8.0 Hz, 2H), 7.17(d, *J*=7.6 Hz, 2H), 7.23—7.25(m, 1H), 7.28(d, *J*=7.6 Hz, 2H). ^{13}C NMR($CDCl_3$, 100 MHz), *δ*: 21.1, 29.3, 36.3, 38.6, 54.2, 126.7, 127.4, 128.4(2C), 129.1(2C), 129.2(4C), 136.4, 137.7, 141.3, 163.4, 195.7. HRMS, *m*/*z* cacld. for $C_{20}H_{21}OS_2^+$([M+H]$^+$): 341.1028; found: 341.1025.

3-(1,3-Dithiolan-2-ylidene)-4-phenyl-4-*m*-tolylbutan-2-one(**3**c): a white solid; m. p. 175—176 °C. ^{1}H NMR($CDCl_3$, 400 MHz), *δ*: 1.86(s, 3H), 2.31(s, 3H), 3.24—3.30(m, 4H), 5.81(s, 1H), 6.96(d, *J*=8.0 Hz, 1H), 7.00(s, 1H), 7.06(d, *J*=7.6 Hz, 1H), 7.17—7.21(m, 3H), 7.25(d, *J*=7.6 Hz, 1H), 7.29(d, *J*=7.6 Hz, 2H). ^{13}C NMR($CDCl_3$, 100 MHz), *δ*: 21.6, 29.3, 36.3, 38.6, 54.5, 126.3, 126.7, 127.4, 127.5, 128.3, 128.4(2C), 129.2(2C), 129.9, 138.0, 140.9, 141.2, 164.1, 195.7. HRMS, *m*/*z* cacld. for $C_{20}H_{21}OS_2^+$([M+H]$^+$): 341.1028; found: 341.1031.

3-(1,3-Dithiolan-2-ylidene)-4-phenyl-4-*o*-tolylbutan-2-one(**3**d): a white solid; m. p. 143—144 °C. ^{1}H NMR($CDCl_3$, 400 MHz), *δ*: 1.84(s, 3H), 2.20(s, 3H), 3.19—3.30(m, 4H), 5.74(s, 1H), 7.00(d, *J*=7.6 Hz, 1H), 7.08(d, *J*=7.3 Hz, 2H), 7.12—7.15(m, 1H), 7.19—7.30(m, 5H). ^{13}C NMR($CDCl_3$, 100 MHz), *δ*: 19.7, 29.1, 36.5, 38.4, 52.4, 126.1, 126.7, 127.0, 127.1, 128.5(2C), 129.1(3C), 130.5, 137.6, 139.2, 141.2, 163.6, 195.7. HRMS, *m*/*z* cacld. for $C_{20}H_{21}OS_2^+$([M+H]$^+$): 341.1028; found: 341.1034.

4-(4-Chlorophenyl)-3-(1,3-dithiolan-2-ylidene)-4-phenylbutan-2-one(**3**e): a colorless liquid. ^{1}H NMR($CDCl_3$, 400 MHz), *δ*: 1.87(s, 3H), 2.94(s, 3H), 3.23—3.27(m, 2H), 3.29—3.32(m, 2H), 5.79(s, 1H), 7.11—7.17(m, 4H), 7.27—7.33(m, 5H). ^{13}C NMR($CDCl_3$, 100 MHz), *δ*: 29.2, 36.4, 38.6, 53.9, 126.8, 126.9(2C), 128.5, 128.6(2C), 129.1(2C), 130.6(2C), 132.6, 139.5, 140.5, 164.6, 195.3. HRMS, *m*/*z* cacld. for $C_{19}H_{18}ClOS_2^+$([M+H]$^+$): 361.0482; found: 361.0488.

Ethyl 2-[(Bis(ethylthio)methylene]-4-(1,3-dithiolan-2-ylidene)-3-methyl-5-oxohexanoate(**3**g): a white solid; m. p. 70—71 °C. ^{1}H NMR($CDCl_3$, 400 MHz), *δ*: 1.17—1.27(m, 6H), 1.29—1.36(m, 3H), 1.46(d, *J*=7.3 Hz, 3H), 2.35(s, 3H), 2.72—2.77(m, 4H), 3.25—3.30(m, 4H), 4.16—4.27(m, 2H), 4.31—4.37(m, 1H). ^{13}C NMR($CDCl_3$, 100 MHz), *δ*: 14.1, 14.6, 15.3, 17.7, 27.4, 28.2, 28.6, 36.5, 38.3, 41.1, 61.0, 127.4, 133.0, 145.2,160.8, 167.7, 194.8. HRMS, *m*/*z* cacld. for $C_{17}H_{27}O_3S_4^+$ ([M+H]$^+$): 407.0838; found: 407.0843.

4-(4-Bromophenyl)-3-(1,3-dithiolan-2-ylidene)pentan-2-one(**3**j): a colorless liquid. ^{1}H NMR($CDCl_3$, 400 MHz), *δ*: 1.64(d, *J*=7.2 Hz, 3H), 1.90(s, 3H), 3.30—3.35(m, 4H), 4.41—4.46(m, 1H), 6.96(d, *J*=8.0 Hz, 1H), 7.00(s, 1H), 7.14(d, *J*=8.4 Hz, 2H), 7.41(d, *J*=8.5 Hz, 2H). ^{13}C NMR($CDCl_3$, 100 MHz), *δ*: 16.4, 28.6, 35.9, 38.9, 42.1, 120.1, 128.7(2C), 129.0, 131.5(2C), 142.3, 162.4, 194.8. HRMS, *m*/*z* cacld. for $C_{14}H_{16}BrOS_2^+$([M+H]$^+$): 342.9821; found: 342.9826.

2-(1,3-Dithiolan-2-ylidene)-1,3,3-triphenylpropan-1-one (**3**k): a white solid; m. p. 144—145 °C. ^{1}H NMR($CDCl_3$, 400 MHz), *δ*: 3.20—3.28(m, 4H), 5.59(s, 1H), 7.17—7.19(m, 2H), 7.20—7.29(m, 8H), 7.31(d, *J*=7.7 Hz, 2H), 7.39—7.43(m, 1H), 7.54(d, *J*=8.4 Hz, 2H). ^{13}C NMR($CDCl_3$, 100 MHz), *δ*: 37.6, 38.8, 56.6, 126.5(2C), 128.1(4C), 128.3(2C), 128.6(2C), 129.6(4C), 131.6(2C), 139.0, 141.1(2C), 154.7, 195.3. HRMS, *m*/*z* cacld. for $C_{24}H_{21}OS_2^+$([M+H]$^+$): 389.1028; found: 389.1034.

2-(1,3-Dithiolan-2-ylidene)-3,3-diphenyl-1-*p*-tolylpropan-1-one(**3**l): a white solid; m. p. 126—127 °C. ^{1}H NMR($CDCl_3$, 400 MHz), *δ*: 2.33(s, 3H), 3.16—3.22(m, 4H), 5.56(s, 1H), 7.11(d, *J*=8.0 Hz, 2H), 7.15(t, 2H), 7.22(t, 4H), 7.28(d, *J*=7.4 Hz, 4H), 7.50(d, *J*=8.1 Hz, 2H). ^{13}C NMR($CDCl_3$, 100 MHz), *δ*: 21.7, 37.5, 38.8, 57.0, 126.5(2C), 128.1(4C), 128.2, 129.1(2C), 129.2(2C), 129.6(4C), 136.0, 141.2(2C), 142.7, 152.0, 195.2. HRMS, *m*/*z* cacld. for $C_{25}H_{23}OS_2^+$([M+H]$^+$): 403.1185; found: 403.1183.

2-(1,3-Dithiolan-2-ylidene)-3,3-diphenyl-1-*m*-tolylpropan-1-one(**3**m): a white solid; m. p. 97—98 °C. ^{1}H NMR($CDCl_3$, 400 MHz), *δ*: 2.27(s, 3H), 3.17—3.23(m, 4H), 5.57(s, 1H), 7.15—7.21(m, 5H), 7.23—7.26(m, 7H), 7.30(s, 1H), 7.33(d, *J*=7.4 Hz, 1H). ^{13}C NMR($CDCl_3$, 100 MHz), *δ*: 21.3, 37.5, 38.7, 56.5, 125.8, 126.5(2C), 128.0, 128.1(5C), 129.0, 129.6(4C), 132.3, 138.0, 139.0, 141.1(2C), 155.0, 195.5. HRMS, *m*/*z* cacld. for $C_{25}H_{23}OS_2^+$([M+H]$^+$): 403.1185; found: 403.1187.

2-(1,3-Dithiolan-2-ylidene)-3,3-diphenyl-1-*o*-tolylpropan-1-one(**3**n): a white solid; m. p. 128—129 °C. ^{1}H NMR($CDCl_3$, 400 MHz), *δ*: 2.09(s, 3H), 3.20(s, 4H), 5.54(s, 1H), 6.97(d, *J*=7.5 Hz, 1H), 7.05(t, 1H), 7.10—7.13(m, 4 H), 7.18—7.26(m, 8H). ^{13}C NMR($CDCl_3$, 100 MHz), *δ*: 19.2, 37.7, 38.2, 54.8, 125.2, 126.2, 126.5(2C), 128.0, 128.2(4C), 129.2, 129.6(4C), 130.7, 135.7, 140.3, 140.9(2C), 164.3, 195.8. HRMS, *m*/*z* cacld. for $C_{25}H_{23}OS_2^+$([M+H]$^+$): 403.1185; found: 403.1186.

1-(4-Bromophenyl)-2-(1,3-dithiolan-2-ylidene)-3,3-diphenylpropan-1-one(**3**o): a white solid; m. p. 156—157 °C. ^{1}H NMR($CDCl_3$, 400 MHz), *δ*: 3.23—3.30(m, 4H), 5.55(s, 1H), 7.16—7.20(m, 2H), 7.24(s, 5H), 7.25(s, 3H), 7.39—7.45(m, 4H). ^{13}C NMR($CDCl_3$, 100 MHz), *δ*: 37.6, 38.8, 56.7, 126.6(2C), 127.5, 128.2(4C), 129.5(4C), 130.3(2C), 131.6(2C), 137.7, 140.9(2C), 154.9, 194.2. HRMS, *m*/*z* cacld. for $C_{24}H_{20}BrOS_2^+$([M+H]$^+$): 467.0133; found: 467.0128.

(E)-4-(1,3-Dithiolan-2-ylidene)-5,5-diphenyl-1-(thiophen-2-yl)pent-1-en-3-one(**3**q): a yellow solid; m. p. 170—171 °C. ^{1}H NMR($CDCl_3$, 400 MHz), *δ*: 3.23—3.30(m, 4H), 5.91(s, 1H), 6.50(d, *J*=15.1 Hz, 1H), 6.91(d, *J*=8.6 Hz, 1H), 7.01(s, 1H), 7.20—7.25(m, 7H). 7.32(t, 4H), 7.58(d, *J*=15.1 Hz, 1H). ^{13}C NMR($CDCl_3$, 100 MHz), *δ*: 36.1, 38.9, 55.0, 124.6, 126.7(2C), 127.6, 127.8, 127.9, 128.6(4C), 129.0(4C), 130.1, 133.7, 141.2, 141.5(2C), 164.9, 186.2. HRMS, *m*/*z* cacld. for $C_{24}H_{21}OS_3^+$([M+H]$^+$): 421.0749; found: 421.0748.

(*E*)-4-(1,3-Dithiolan-2-ylidene)-1-(furan-2-yl)-5,5-

diphenylpent-1-en-3-one(**3r**): a yellow solid; m. p. 155—156 °C. ^{1}H NMR($CDCl_3$, 400 MHz), δ: 3.30—3.34(m, 4H), 5.91(s, 1H), 6.35(d, J=17.9 Hz, 1H), 6.62(d, J=15.2 Hz, 1H), 7.20—7.25(m, 7H). 7.28—7.32(m, 5H), 7.36(s, 1H). ^{13}C NMR($CDCl_3$, 100 MHz), δ: 36.2, 38.8, 54.8, 112.1, 114.1, 123.0, 126.7(2C), 127.8, 127.9, 128.3, 128.4(4C), 129.2(4C), 141.4, 144.1, 152.2, 164.4, 186.6. HRMS, *m*/*z* cacld. for $C_{24}H_{21}O_2S_2^+$([M+H]$^+$): 405.0977; found: 405.0983.

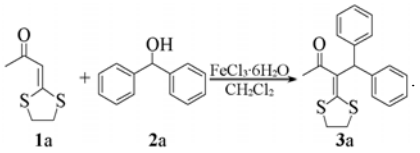
Methyl 2-(1,3-dithiolan-2-ylidene)-3,3-diphenyl propanoate(**3u**): a white solid; m. p. 124—125 °C. ^{1}H NMR($CDCl_3$, 400 MHz), δ: 3.31—3.38(m, 4H), 3.49(s, 3H), 5.65(s, 1H), 7.19—7.22(m, 6H), 7.25—7.29(m, 4H), ^{13}C NMR($CDCl_3$, 100 MHz), δ: 37.1, 38.6, 51.2, 54.9, 118.9, 126.3(2C), 128.0(4C), 129.1(4C), 141.7(2C), 162.1, 166.9. HRMS, *m*/*z* cacld. for $C_{19}H_{19}O_2S_2^+$([M+H]$^+$): 343.0821; found: 343.0827.

3 Results and Discussion

On the basis of our previous researches[34,35], we chose $FeCl_3{\cdot}6H_2O$ as catalyst and CH_2Cl_2 as solvent to investigate the Friedel-Crafts alkylation of ketene dithioacetals with alcohols. To optimize the catalyst loading and reaction temperature, we carried out reactions with (1,3-dithiolan-2-ylidene)-propan-2-one(**1a**) and diphenylme-thanol(**2a**) as substrates. The results are summarized in Table 1.

Table 1 Screening of the reaction conditions[a]

Entry	$FeCl_3{\cdot}6H_2O$(%, molar fraction)	Solvent	Temperature/ °C	Time/h	Yield[b] (%)
1	10	CH_2Cl_2	r. t.	8	96
2	10	CH_2Cl_2	Reflux	0.6	95
3	5	CH_2Cl_2	r. t.	12	95
4	5	CH_2Cl_2	Reflux	1	97
5	2.5	CH_2Cl_2	r. t.	48	67
6	2.5	CH_2Cl_2	Reflux	6	75

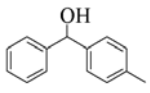
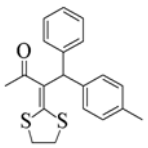
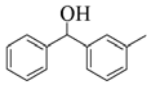
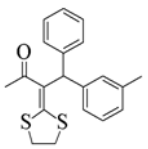
a. 

1a **2a** **3a**. Reagents and conditions: **1a**(0.5 mmol), **2a**(0.75 mmol), CH_2Cl_2 solvent(1 mL); *b*. isolated yield.

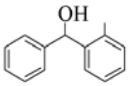
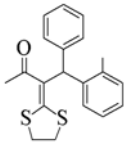
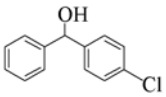
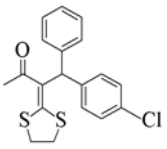
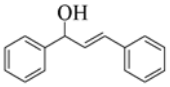
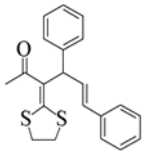
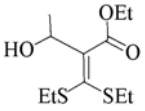
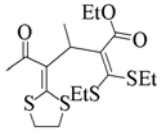
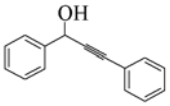
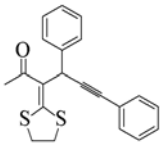
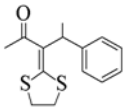
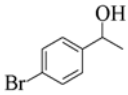
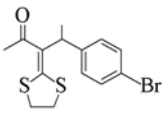
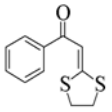
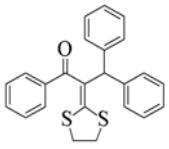
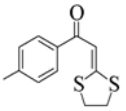
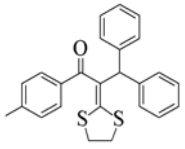
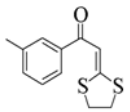
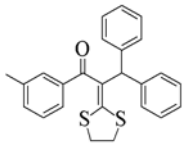
Apparently, the amount of $FeCl_3{\cdot}6H_2O$ has a dramatic influence on this reaction. It was found that with 10% or 5% of $FeCl_3{\cdot}6H_2O$ as catalyst, the target Friedel-Crafts alkylation of ketene dithioacetals with alcohols proceeded efficiently at room temperature or reflux temperature, thereby affording the desired product **3a** in nearly quantitative yields(Entries 1—4, Table 1). Whereas, the reaction efficiency is diminished in the presence of 2.5% of $FeCl_3{\cdot}6H_2O$ at room temperature or reflux temperature(Entries 5 and 6, Table 1). So, the reaction conditions were optimized as follows: with 5% $FeCl_3{\cdot}6H_2O$ as catalyst, CH_2Cl_2 as solvent and at room temperature(A) or reflux temperature(B).

Next, we investigatd the scope of the reaction under the optimal reaction conditions. The results are summarized in Table 2. Initially, we checked the scope of the Friedel-Crafts alkylation in terms of alcohols. We found that a variety of alcohols such as diarylmethanols **2a—2e**, allylic alcohols **2f** and **2g**, propargylic alcohol **2h** and benzylic alcohols **2i** and **2j** reacted efficiently with ketene dithioacetal **1a**, affording the alkylated ketene dithioacetals **3a—3j** in quantitate yields (Entries 1—10, Table 2). Later, we explored the reaction outcome with different ketene dithioacetals(Entries 11—21, Table 2). It was found that divergent ketene dithioacetals such as 2-(1,3-dithiolan-2-ylidene)-1-aryl-ethanones(**1b—1f**), (*E*)-1-(1,3-dithiolan-2-ylidene)-4-aryl-but-3-en-2-ones(**1g—1i**), 2-(1,3-dithiolan-2-ylidene)acetamides(**1j**), 3-(1,3-dithiolan-2-ylidene)-2-oxo-propanenitrile(**1k**) and methyl 2-(1,3-dithiolan-2-ylidene) acetate(**1l**) are suitable for the Friedel-Crafts alkylation with alcohols. The reactions with dipenylmethanol **2a** gave the corresponding alkylated ketene dithioacetals **3k—3u** in excellent yields. It is noteworthy that the reaction of heteroaryl-alkenoyl ketene dithioacetals **1h** and **1i** with dipenylmethanol **2a** exclusively formed the desired products **3q** and **3r** respectively in good yields. In these reactions, the by-product of Friedel-Crafts alkylation in hetero-arylates was not detected(Entries 17 and 18, Table 2). Furthermore, we examined the reaction outcome of 1-(1,3-dithian-2-ylidene) propan-2-one **1m** with alcohols **2a** or **2h**, and found that the reactions proceeded successfully at room temperature(condition A) or reflux temperature(condition B), thereby affording the target products **3v** or **3w** in high yields(Entries 22, 23, Table 2).

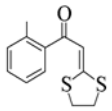
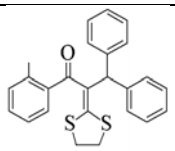
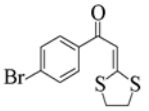
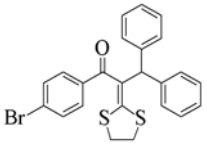
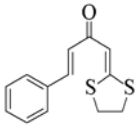
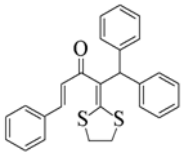
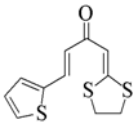
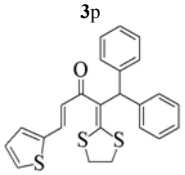
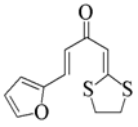
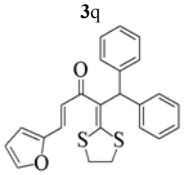
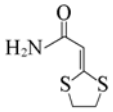
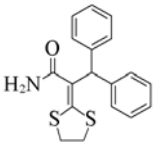
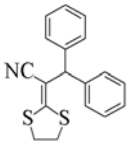
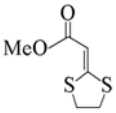
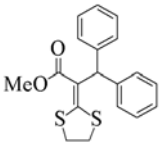
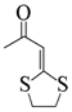
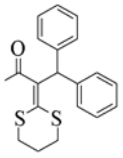
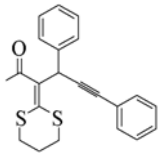
Table 2 $FeCl_3{\cdot}6H_2O$ catalyzed Friedel-Crafts alkylation of cyclic ketene dithioacetals 1 with alcohols 2[a]

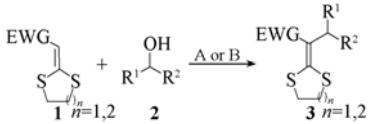
Entry	**1**	**2**	Condition	Time/h	**3**	Yield[b](%)
1	**1a**	**2a**	A B	12 1	**3a**	95 97
2	**1a**		A B	12 1		96 95
		2b			**3b**	
3	**1a**		A B	12 1		97 96
		2c			**3c**	

To be continued on the next page.

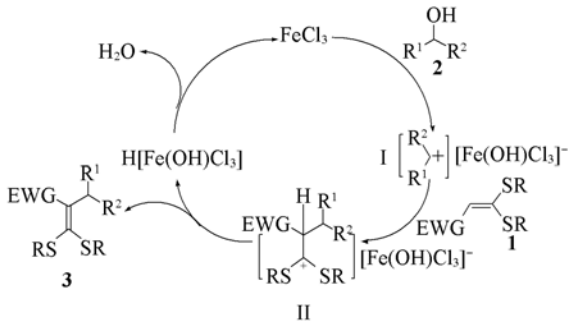
Entry	1	2	Condition	Time/h	3	Yield[b](%)
4	**1**a	 **2**d	A B	12 1	 **3**d	94 95
5	**1**a	 **2**e	A B	12 1	 **3**e	96 94
6	**1**a	 **2**f	A B	12 1	 **3**f	92 90
7	**1**a	 **2**g	A B	12 1	 **3**g	96 97
8	**1**a	 **2**h	A B	12 1	 **3**h	90 89
9	**1**a	 **2**i	B	4	 **3**i	85
10	**1**a	 **2**j	B	4	 **3**j	87
11	 **1**b	**2**a	A B	16 1.5	 **3**k	96 94
12	 **1**c	**2**a	A B	16 1.5	 **3**l	95 96
13	 **1**d	**2**a	A B	16 1.5	 **3**m	93 92

To be continued on the next page.

Entry	1	2	Condition	Time/h	3	Yield[b](%)
14	 **1**e	**2**a	A B	16 1.5	 **3**n	92 90
15	 **1**f	**2**a	A B	16 1.5	 **3**o	94 95
16	 **1**g	**2**a	B	7	 **3**p	77
17	 **1**h	**2**a	B	8	 **3**q	81
18	 **1**i	**2**a	B	8	 **3**r	74
19	 **1**j	**2**a	B	5	 **3**s	89
20	 **1**k	**2**a	A B	10 1	 **3**t	93 94
21	 **1**l	**2**a	A B	14 1.5	 **3**u	93 94
22	 **1**m	**2**a	A B	14 1	 **3**v	91 93
23	**1**m	**2**h	A B	15 1	 **3**w	92 90

a.  , with 5% $FeCl_3 \cdot 6H_2O$ as catalyst in CH_2Cl_2 and at r.t. (A) or reflux temperature(B); *b*. isolated yield.

Based on our previous reports[34,35] and the present experimental results, we proposed a possible mechanism(Scheme 1). It is clear that the reaction of compounds **1** and **2** is presumably initiated by the formation of carbocation I from alcohol **2**, by the removal of hydroxyl group of **2** with $FeCl_3$. Nucleophilic attack at the cationic carbon atom of I by α-carbon of **1** forms the more stable intermediate II stabilized by the two adjacent alkylthio groups. α-Hydrogen elimination of II affords the desired compound **3** as well as $H[Fe(OH)Cl_3]$ species which can further regenerate $FeCl_3$ and complete the catalytic cycle.



Scheme 1 Proposed mechanism for $FeCl_3·6H_2O$ catalyzed Friedel-Crafts alkylation of compound 1 with compound 2

4 Conclusions

In summary, we developed a novel and efficient $FeCl_3·6H_2O$-catalyzed Friedel-Crafts alkylation of actived internal olefins, *i. e.* ketene dithioacetals **1** with alcohols **2**, for the synthesis of alkylated ketene dithioacetals **3** in excellent yields. Compared to conventional methods, the advantages such as good generality of the protocol, the use of inexpensive, nontoxic, moisture insensitive and environmentally friendly $FeCl_3·6H_2O$ as catalyst, and the use of lower amount of catalyst made the reaction very attractive.

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