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Lithium bromide/triethylamine promoted tandem cycloaddition–oxidation reaction: A convenient access to 3-trifluoroacetyl pyrroles from N-alkylidene 2-amino esters and β-trifluoroacetyl vinyl ethyl ether

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ABSTRACT

A convenient lithium bromide/triethylamine promoted tandem cycloaddition–oxidation reaction was developed to afford 3-trifluoroacetyl pyrroles in moderate to good yields from N-alkylidene 2-amino esters and β-trifluoroacetyl vinyl ethyl ether.

1. Introduction

Owing to the increasing importance of fluorine-containing heterocycles in the fields of biology and pharmacology, the development of efficient methods for the synthesis of these motifs have long been an interesting subject [1]. Among those well-developed methodologies for constructing 5-membered heterocycles, 1,3-dipolar cycloaddition represents one of the most versatile tools [2]. β-Trifluoroacetyl vinyl ethers were first prepared in 1967 [3], and the existence of polarized C=C and reactive trifluoroacetyl group have made them widely used as building blocks for the synthesis of fluorine-containing heterocycles [4].

Recently, 1,3-dipolar cycloaddition reactions have been developed based on N-alkylidene 2-amino esters, which are known as stabilized azomethine yields. Many catalyst such as Cu(I), Ag(I), lithium salts, Fesulphos, organocatalysts and composite catalysts are commonly used in the reactions between N-alkylidene 2-amino esters and electron-deficient or polarized double bond in a stereoselective and regioselective manner [5a–f]. Considering about the efficiency and versatility of the reaction, it becomes one of the most convergent and practical approaches to the synthesis of pyrrolidines and proline derivatives. Herein, we report a convenient access to 3-trifluoroacetyl pyrroles from easily available N-alkylidene 2-amino esters and β-trifluoroacetyl vinyl ethyl ether.

2. Results and discussion

Initial study was investigated from (*E*)-4-ethoxy-1,1,1-trifluorobut-3-en-2-one **1** and (*E*)-methyl 2-(benzylideneamino)acetate **2a** in the presence of one equivalent of pyridine (Table 1, entry 1). However, the reaction proceeded rather tediously. And no significant acceleration was observed with addition of $AgNO_3$ [6], which may be due to the low solubility of $AgNO_3$ in THF. When lithium bromide hydrate was employed as catalyst, to our delight, the reaction could be finished within 3 h. Investigation of the ^1H NMR and ^{19}F NMR suggested that the ethoxyl group was eliminated during the reaction while trifluoroacyl group remained intact (−73.7 ppm). Moreover, the mass spectrum indicated a loss of two H atoms of the cycloaddition product, which was also proved by the ^1H NMR. Concerning with other spectra, the structure was determined as a pyrrole cycle [7]. It should be noted that the synthesis of 3-trifluoroacetyl substituted pyrroles were normally reported by multiple-step reactions, either through a protection–acylation–deprotection or addition–oxidation process [8a,b].

In order to improve the yield, the effect of bases was investigated and the results are summarized in Table 1. It is

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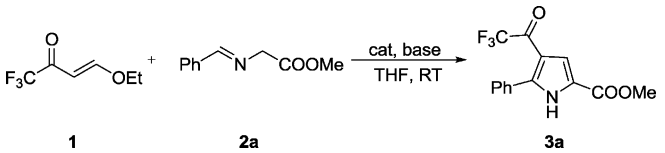
Table 1
Effect of bases on the reaction azomethine yield **2a** and **1**.



Entry	Cat/base	Yield (%)[a]
1	$AgNO_3$/pyridine	N.R.
2	$LiBr{\cdot}H_2O$/pyridine	15
3	$LiBr{\cdot}H_2O$/quinine	24
4	$LiBr{\cdot}H_2O$/N,N-dimethylaniline	Trace
5	$LiBr{\cdot}H_2O$/N,N-diethylaniline	12
6	$LiBr{\cdot}H_2O/NEt_3$	73
7	$LiBr{\cdot}H_2O$/NaOAc	18
8	$LiBr{\cdot}H_2O/NaCO_3$	Trace
9	$LiBr{\cdot}H_2O/LiCO_3$	3
10	$LiBr{\cdot}H_2O/K_2CO_3$	30
11	$LiBr{\cdot}H_2O$/NaOH	77
12	$LiBr{\cdot}H_2O$/KOH	63

[a] Determined by ^{19}F NMR except entry 2, adding 0.5 mmol trifluoromethylbenzene as standard.

obvious that stronger base led to a relatively higher yield whether it is organic or inorganic. In view of the feasibility and efficiency, triethylamine was chosen as optimal base (entry 6), although KOH and NaOH both led to a satisfactory yield (entries 11 and 12).

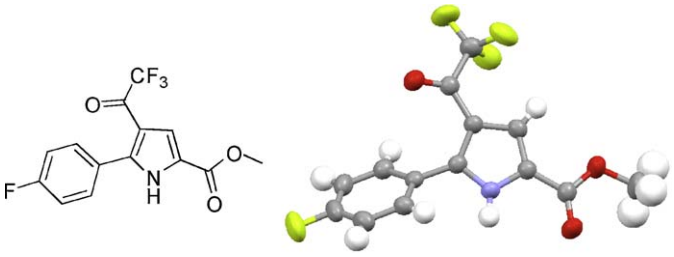


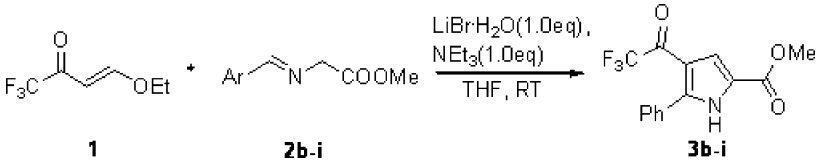
Fig. 1. Molecular structure of compound **3e**.

With the optimized reaction condition in hand, we then extended the reaction with a series of N-alkylidene 2-amino esters. All the results are summarized in Table 2. It is implied that with an EWG attached on Ph, the reaction proceeded faster and led to a higher yield.

The molecular structure of **3e** was further confirmed by an X-ray crystal structure analysis (Fig. 1).

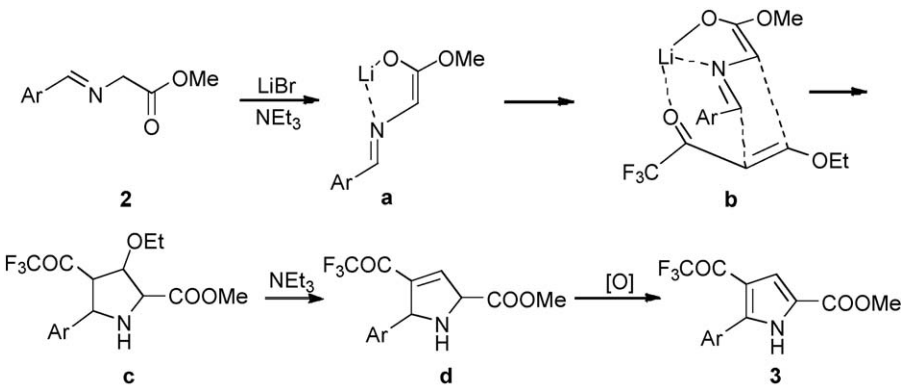
The pyrrole products might be generated as shown in Scheme 1. Lithium enolate **a** was generated from **2** in the presence of LiBr and NEt_3. Then, under the chelation effect of lithium [5d], which highly contributed to the acceleration of the reaction, concerted 1,3-dipolar cycloaddition led to **c**. The following elimination of ethanol afforded **d** [9]. Then, as a result of the tendency of aromatization [1,10], spontaneous air oxidation led to a substituted pyrrole. When there is an EWG attached on Ph, the chelation complex **b** can be generated easier than there is an EDG.

Table 2
Synthesis of CF_3CO-bearing Pyrroles.



Entry	Ar	3b–i	Time (h)	Yield (%)[a]
1	4-MeO–Ph (**2b**)	**3b**	18	62
2	4-Br–Ph (**2c**)	**3c**	12	59
3	4-Cl–Ph (**2d**)	**3d**	3	73
4	4-F–Ph (**2e**)	**3e**	3	58
5	2-F–Ph (**2f**)	**3f**	10	75
6	3-F–Ph (**2g**)	**3g**	4	77
7	4-CF_3–Ph (**2h**)	**3h**	4	81
8	4-N,N-dimethylamino–Ph (**2i**)	**3i**	20	47

[a] Isolated yield.



Scheme 1. Mechanism of the cycloaddition–oxidation.

3. Conclusion

In conclusion, we have developed a convenient tandem cycloaddition–oxidation reaction in the presence of lithium bromide. 3-Trifluoroacetyl substituted pyrroles could be synthesized in good yields from easily available N-alkylidene 2-amino esters and β-trifluoroacetyl vinyl ethyl ethers. The mild condition and satisfactory yield will provide this reaction as a useful method for the construction of chemical library with pyrrole motifs.

4. Experimental

Melting points are measured on a Temp-Melt apparatus and are uncorrected. ^{1}H (300 MHz), ^{13}C NMR (75 MHz) and ^{19}F NMR (282 MHz) spectra were recorded on a Bruker AM-300 ultra shield, 300 MHz, high performance digital FT-NMR spectrometer with Me_4Si and $CFCl_3$ as the internal and external standards, respectively. ^{13}C NMR (100 MHz) spectra were recorded on a Bruker AV-400 ultra shield plus, 400 MHz, high performance digital FT-NMR spectrometer with Me_4Si as the internal standard. FTIR spectra were obtained with a Nicolet AV-360 spectrophotometer. Low resolution mass spectra (LRMS) and high resolution mass spectra (HRMS) were obtained on a Finnigan GC–MS 4021 and a Finnigan MAT-8430 instrument using the electron impact ionization technique (70 eV) or electrospray ionization. Elemental analyses were performed by this institute. Single crystal X-ray structure analysis was performed on a Bruker P4 instrument. All solvents and reagents were used without further purification unless otherwise stated.

4.1. General procedure

The α-imino esters were prepared following the literature procedure [5a].

To a single-necked flask containing THF (15 mL) was added 4-ethoxy-1,1,1-trifluorobut-3-en-2-one **1** (504 mg, 3 mmol), corresponding N-alkylidene 2-amino ester **2** (3 mmol), lithium bromide hydrate (315 mg, 3 mmol) and triethylamine (303 mg, 3 mmol) in one portion at room temperature. When the reaction was completed monitored by TLC, the reaction was quenched by saturated NH_4Cl (15 mL) and extracted by ethyl ether (30 mL × 3), and the organic layer was dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by flash chromatography on silica gel (ethyl acetate–*n*-hexane, 1:5) to afford **3**.

4.1.1. Methyl 5-phenyl-4-(2,2,2-trifluoroacetyl)-1H-pyrrole-2-carboxylate **3a**

Colorless crystals. Mp = 183 °C. FTIR (KBr) cm^{-1}: 3260, 1691, 1567, 1462, 1211, 1137, 895, 762, 695. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.96 (br s, 1H, NH), 7.64–7.61 (m, 2H, ArH), 7.49–7.45 (m, 4H, ArH and $H_{pyrrole}$), 3.86 (s, 3H, COOCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.6 (q, J = 34.0 Hz), 161.0, 144.6, 130.2, 129.6, 129.1, 128.5, 123.2, 118.1 (q, J = 4.0 Hz), 116.7 (q, J = 290.0 Hz), 114.4, 52.2. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −73.7 (s). ESI-MS: m/z $[M+H]^+$ = 298, m/z $[M+NH_4]^+$ = 315, m/z $[M+Na]^+$ = 320. HRMS (ESI): m/z calcd. for $C_{14}H_{10}F_3N_1O_3$ [M+Na]: 320.0505; found: 320.0504.

4.1.2. Methyl 5-(4-methoxyphenyl)-4-(2,2,2-trifluoroacetyl)-1H-pyrrole-2-carboxylate **3b**

Colorless crystals. Mp = 171–172 °C. FTIR (KBr) cm^{-1}: 3280, 2444, 1746, 1689, 1611, 1545, 1442, 892, 758, 734. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.65 (br s, 1H, NH), 7.60 (d, 2H, J = 9.0 Hz, ArH), 7.44 (s, 1H, $H_{pyrrole}$), 6.99 (d, 2H, J = 9.0 Hz, ArH), 3.90 (s, 3H, Ar–OCH_3), 3.87 (s, 3H, COOCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.6 (q, J = 33.0 Hz), 161.1, 160.1, 145.3, 131.2, 123.7, 121.9, 117.3 (q, J = 4.0 Hz), 117.1 (q, J = 290.0 Hz), 113.4, 113.2, 54.9, 51.2. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −73.6 (s). ESI-MS: m/z $[M+H]^+$ = 328. HRMS: m/z calcd. for $C_{15}H_{12}F_3N_1O_4$ [M+Na]: 350.0611; found: 350.0614.

4.1.3. Methyl 5-(4-bromophenyl)-4-(2,2,2-trifluoroacetyl)-1H-pyrrole-2-carboxylate **3c**

Colorless crystals. Mp = 176 °C. FTIR (KBr) cm^{-1}: 3258, 2958, 1689, 1571, 899, 782, 720. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.15 (br s, 1H, NH), 7.61 (d, 2H, J = 8.7 Hz, ArH), 7.50 (d, 2H, J = 8.7 Hz, ArH), 7.45 (s, 1H, $H_{pyrrole}$), 3.85 (s, 3H, COOCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.3 (q, J = 34.0 Hz), 159.9, 143.5, 131.7, 131.1, 129.0, 124.2, 123.6, 117.2 (q, J = 4.0 Hz), 116.9 (q, J = 290.0 Hz), 113.9, 51.3. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −73.73 (s). ESI-MS: m/z $[M-H]^-$ = 374:376 = 1:1. HRMS: m/z $[M]^+$ calcd. for $C_{14}H_9Br_1F_3N_1O_3$: 374.9718, found: 374.9721; calcd.: 376.9697, found: 376.9699.

4.1.4. Methyl 5-(4-chlorophenyl)-4-(2,2,2-trifluoroacetyl)-1H-pyrrole-2-carboxylate **3d**

Colorless crystals. Mp = 179–180 °C. FTIR (KBr) cm^{-1}: 3259, 2964, 1915, 1704, 152, 1345, 1029, 1004, 898, 860, 784, 645. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.6 (br s, 1H, NH), 7.57 (d, 2H, J = 6.6 Hz, ArH), 7.43 (m, 3H, ArH and $H_{pyrrole}$), 3.78 (s, 3H, COOCH_3). ^{13}C NMR (100 MHz, acetone-d_6): δ = 174.8 (q, J = 34.0 Hz), 160.0, 143.6, 135.3, 131.4, 128.6, 128.1, 124.3, 117.3 (q, J = 4.0 Hz), 116.9 (q, J = 290.0 Hz), 112.6, 51.3. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −73.8 (s). ESI-MS: m/z $[M+H]^+$ = 332:334 = 3:1. HRMS: m/z $[M]^+$ calcd. for $C_{14}H_9N_1O_3Cl_1F_3$: 331.0223; found: 331.0220.

4.1.5. Methyl 5-(4-fluorophenyl)-4-(2,2,2-trifluoroacetyl)-1H-pyrrole-2-carboxylate **3e**

Colorless crystals. Mp = 189–190 °C. FTIR (KBr) cm^{-1}: 3354, 2968, 1713, 1681, 1570, 90, 843, 761, 736. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.17 (br s, 1H, NH), 7.63 (dd, 2H, J = 5.7, 3.0 Hz, ArH), 7.44 (s, 1H, $H_{pyrrole}$), 7.16 (t, 2H, J = 8.1 Hz, ArH), 3.83 (s, 3H, COOCH_3). ^{19}F NMR (282 MHz, $CDCl_3$): δ = −73.9 (s, 3F, CF_3CO), 110.0 (t, 1F, J = 8.5 Hz, ArF). ESI-MS: m/z (%) = 315 (M^+, 42), 284 (6), 246 (34), 214 (100), 158 (26). Anal. Calcd. for $C_{14}H_9F_4NO_3$: C, 53.34; H, 2.88; N, 4.44. Found: C, 53.50; H, 2.92; N, 4.42.

Structural parameters for **3e**: $C_{14}H_9F_4NO_3$, yellow block, crystal dimension 0.26 mm × 0.22 mm × 0.15 mm, monoclinic, space group $P2(1)/n$, a = 13.355 (2) Å, b = 7.6243 (14) Å, c = 13.642 (2) Å, α = 90.00°, β = 109.211 (2)°, γ = 90.00°, V = 1311.7 (4) Å^3, Dc = 1.596 Mg/m^3, λ(Mo-Ka) = 0.71073 Å. CCDC reference number 748896.

4.1.6. Methyl 5-(2-fluorophenyl)-4-(2,2,2-trifluoroacetyl)-1H-pyrrole-2-carboxylate **3f**

Colorless crystals. Mp = 170 °C. FTIR (KBr) cm^{-1}: 3248, 2958, 1700, 1620, 1572, 1005, 900, 801, 759, 677. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.73 (br s, 1H, NH), 7.67–7.54 (m, 3H, ArH and $H_{pyrrole}$), 7.37–7.29 (m, 2H, ArH), 3.86 (s, 3H, COOCH_3). ^{13}C NMR (100 MHz, acetone-d_6): δ 175.1 (q, J = 35.0 Hz), 160.1 (d, J = 247.0 Hz), 160.2, 137.7, 132.1 (d, J = 9.0 Hz), 131.8, 124.6, 124.2 (d, J = 3.0 Hz), 118.2 (d, J = 15.0 Hz), 117.3, 116.7 (q, J = 289.0 Hz), 116.4 (q, J = 4.0 Hz), 115.6 (d, J = 22.0 Hz), 51.7. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −74.2 (s, 3F, CF_3CO), −113.3 (s, 1F, ArF). ESI-MS: m/z (%) = 315 (M^+, 36), 284 (6), 214 (100), 158 (26). HRMS: m/z $[M]^+$ calcd. for $C_{14}H_9N_1O_3F_4$: 315.0519; found: 315.0515.

4.1.7. Methyl 5-(3-fluorophenyl)-4-(2,2,2-trifluoroacetyl)-1H-pyrrole-2-carboxylate **3g**

Colorless crystals. FTIR (KBr) cm^{-1}: 3262, 2964, 1933, 1719, 1570, 902, 786, 786, 643, 603. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.74 (br s, 1H, NH), 7.46–7.39 (m, 3H, ArH), 7.36 (s, 1H, $H_{pyrrole}$), 7.19–7.14 (m, 1H, ArH), 3.77 (s, 3H, COOCH_3). ^{13}C NMR (100 MHz, acetone-d_6):

δ = 174.9 (q, J = 36.0 Hz), 162.2 (d, J = 242.0 Hz), 159.9, 143.2, 132.0 (d, J = 9.0 Hz), 129.9 (d, J = 8.0 Hz), 125.8 (d, J = 3.0 Hz), 124.4, 117.2 (q, J = 4.0 Hz), 116.7 (q, J = 290.0 Hz), 116.6 (d, J = 47.0 Hz), 116.5 (d, J = 3.0 Hz), 114.0, 51.3. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −73.9 (s, 3F, CF_3CO), −112.7 (s, 1F, ArF). ESI-MS: m/z $[M+H]^+$ = 316, m/z $[M+NH_4]^+$ = 333. HRMS: m/z $[M]^+$ calcd. for $C_{14}H_9N_2O_3F_4$: 315.0519; found: 315.0521.

4.1.8. Methyl 4-(2,2,2-trifluoroacetyl)-5-(4-(trifluoromethyl)phenyl)-1H-pyrrole-2-carboxylate **3h**

Colorless crystals. Mp = 181–182 °C. FTIR (KBr) cm^{-1}: 3346, 2968, 1966, 1716, 1678, 1453, 1289, 917, 845, 760, 663. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.71 (br s, 1H, NH), 7.76–7.73 (m, 4H, ArH and $H_{pyrrole}$), 7.47–7.46 (m, 1H, ArH), 3.72 (s, 3H, $COOCH_3$). ^{13}C NMR (100 MHz, acetone-d_6): δ 175.0 (q, J = 34 Hz), 159.9, 142.9, 133.9, 130.8 (q, J = 32 Hz), 130.6, 124.3 (q, J = 270 Hz), 124.8 (q, J = 4 Hz), 124.7, 117.8 (q, J = 290 Hz), 117.2 (q, J = 4 Hz), 114.3, 51.4. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −63.4 (s, 3F, $ArCF_3$), −73.9 (s, 3F, CF_3CO). ESI-MS: m/z $[M+H]^+$ = 366, m/z $[M+NH_4]^+$ = 383. HRMS: m/z $[M]^+$ calcd. for $C_{15}H_9NO_3F_6$: 365.0487; found: 365.0488.

4.1.9. Methyl 5-(4-(dimethylamino)phenyl)-4-(2,2,2-trifluoroacetyl)-1H-pyrrole-2-carboxylate **3i**

Light yellow crystals. Mp = 208–209 °C FTIR (KBr) cm^{-1}: 3276, 2955, 1687, 1610, 1568, 896, 824, 770, 733. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.61 (br s, 1H, NH), 7.57 (d, 2H, J = 8.7 Hz, ArH), 7.42 (s, 1H, $H_{pyrrole}$), 6.75 (d, 2H, J = 8.7 Hz, ArH), 3.89 (s, 3H, $COOCH_3$), 3.04 (s, 6H, $N(CH_3)_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.2 (q, J = 34.0 Hz), 161.2, 151.3, 150.0, 130.2, 117.1 (q, J = 284.0 Hz), 122.3, 118.5 (q, J = 12.0 Hz), 116.8, 113.4, 111.6, 52.1, 40.2. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −73.44 (s). ESI-MS: m/z (%) = 340 (M^+, 62), 308 (100), 183 (88), 119 (35), 91 (12). HRMS: m/z $[M]^+$ calcd. for $C_{16}H_{15}N2O_3F_3$: 340.1035; found: 340.1039.

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