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# First synthesis of unexpected functionalized trifluoromethylated 8-oxa-2,4-diazaspiro[5.5]-undecanes *via* one-pot MCRs†

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Ethyl-7,11-diaryl-9-hydroxy-1,3,5-trioxo-9-(trifluoromethyl)-8-oxa-2,4-diazaspiro[5.5]undecane-10-carboxylate derivatives (4) were synthesized from barbituric acid, aromatic aldehydes and ethyl 4,4,4-trifluoro-3-oxobutanoate *via* a one-pot, multi-component reaction catalyzed by $Et_3N$. The effect of catalyst and temperature on reaction efficiency and yield was investigated. In addition, the treatment of 4 with $SOCl_2$/pyridine in the solvent $CH_3CN$ afforded the corresponding dehydrated products 5. A plausible reaction mechanism for the formation of compounds 4 was presented.

## Introduction

Incorporation of the trifluoromethyl group into organic molecules has attracted significant attention[1] because of the different physical, chemical and biological properties of the trifluoromethyl group. As a consequence, trifluoromethyl-substituted compounds are becoming increasingly important for the development of new agrochemicals and medicines.[2] The $CF_3$ group has a unique size and special electronic properties, and it often imparts increased metabolic stability, elevated lipophilicity and enhanced binding selectivity of bioactive molecules.[3] In recent years, the synthesis of trifluoromethyl heterocycles has been investigated extensively.[4]

Multicomponent reactions (MCRs) are generally defined as one of the most important and useful methods in conventional chemical reactions because they reduce operative steps and enhance synthetic efficiency.[5] MCRs, such as the Biginelli,[6] Passerini,[7] Ugi,[8] and Hantzsch[9] reactions, provide a wide variety of important heterocycles. Therefore, combined with the wide use of MCRs,[10] it is fascinating to apply MCRs in the synthesis of trifluoromethylated heterocycles.

The pyrimidine-2,4,6(1*H*, 3*H*, 5*H*)-trione (barbituric acid) core is an important structural unit present in a variety of products with wide-ranging biological activities and pharmacological properties,[11] especially spiro-compounds with barbituric acid frameworks. As a result, several pyrimidine-2,4,6(1*H*, 3*H*, 5*H*)-trione spiro-derivatives are treated as potent drugs against different kinds of tumours and bacteria such as SKLB016,[12] PUN-286607,[13] 5-[(2*E*)-1-(1*H*-benzimidazol-2-yl)-3-substituted phenyl-prop-2-en-1-ylidene] pyrimidine-2,4,6(1*H*,3*H*,5*H*)-triones[14] and pyrano[2,3-*d*]pyrimidine.[15] In addition, the methylene group of barbituric acid is considerably active in organic synthesis, and the product structures can be divided into three types: monocyclic pyrimidinones,[16] polycyclic benzofuropyrimidinones[17] and dispiropyrimidinones.[18] To continue our ongoing exploration of the synthesis of fluorine-containing heterocycles *via* MCRs based on trifluoromethyl-1,3-dicarbonyl compounds, a versatile fluorine-containing building-block,[19] herein, we wish to report the first example of the synthesis of ethyl-9-hydroxy-1,3,5-trioxo-7,11-diaryl-9-(trifluoromethyl)-8-oxa-2,4-diazaspiro[5.5]-undecane-10-carboxylate derivatives and their dehydration reaction.

## Results and discussion

Initially, we carried out the reaction of pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione **1** and benzaldehyde **2g** with ethyl-4,4,4-trifluoro-3-oxobutanoate **3** in a molar ratio of 1 : 1 : 1 in the presence of a catalytic amount of $Et_3N$ in DMSO at room temperature. TLC analysis showed that the reaction proceeded but ethyl-4,4,4-trifluoro-3-oxobutanoate **3** and barbituric acid **1** were not consumed completely. After the completion of the reaction, general workup afforded a new product **4g** in a yield of about 30%. Surprisingly, according to the $^1H$ NMR spectrum of the newly formed product **4g**, it was clear that two molecules of benzaldehyde **2g** condensed with one molecule of barbituric acid **1** and one molecule of ethyl-4,4,4-trifluoro-3-oxo-butanoate **2** in the new compound. Thus, the molar ratio of ethyl-4,4,4-trifluoro-3-oxobutanoate **3** with pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione **1** and benzaldehyde **2g** was modified to 1 : 1 : 2, and the reaction proceeded under the same reaction conditions. After

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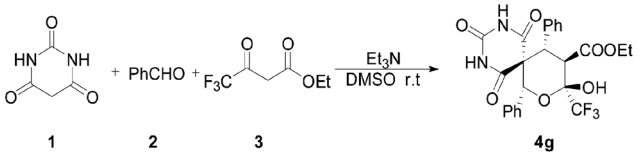
stirring for 12 hours at room temperature, TLC analysis showed that the reaction proceeded smoothly, and a general workup afforded the product **4g** in a yield of 60% as a white solid. The structure of the resultant oxospiro product was quite different from the reported [2,3-*d*]pyrimidine derivatives, which are obtained from the reaction of two similar components with the non-fluorinated beta-keto esters or analogs.[20] This difference was attributed to the unique reactivity of the fluorinated substrate. Note that the reactions in commonly used solvents were not effective because of the poor solubility of barbituric acid.

Based on the abovementioned results, the reaction conditions were optimized to improve the yield by changing catalysts and temperatures. The effects of various organic bases and the amount on the reaction efficiency and yield were first screened (Table 1). As shown in Table 1, only a trace amount of product was formed under reflux conditions. Furthermore, in the absence of a base, no corresponding product formed (entry 1, Table 1); the $Et_3N$ catalyst was superior to most of the other commonly used bases (entry 2–11, Table 1). Clearly, 0.5 equiv. of $Et_3N$ was identified as the optimal catalyst loading with product **4a** isolated in 72% yield (entry 12, Table 1). In addition, it was also found that the prolonged reaction time did not improve product yield (entry 15, Table 1).

Having identified the optimal reaction conditions (entry 12, Table 1), we investigated the scope and limitation of this one-pot, three-component, atom-economical reaction. Various aromatic aldehydes with substituents of different electronic properties reacted smoothly and efficiently under optimal conditions to give the corresponding product **4** in moderate to good yields. The reaction results are summarized in Table 2. In general, it was found that aromatic aldehydes with withdrawing groups gave slightly higher yields than those with weak electron-donating groups (entries 1, 8). However, aromatic aldehydes with strong electron-donating groups, such as 4-methoxybenzaldehyde and 4-hydroxy-3-methoxybenzaldehyde, failed to participate in the reaction. TLC analysis showed that the starting materials remained (entry 13). On the other hand, in the case of 4-nitrobenzaldehyde as a reaction substrate, this compound did not give the expected product but diethyl 2,6-dihydroxy-4-nitro-phenyl-2,6-bis-trifluoromethyl-tetrahydro-pyran-3,5-dicarboxylate **6** was obtained under the reaction conditions (entry 12).[21] Furthermore, aromatic aldehydes with *ortho* substituted groups gave lower yields than those with *para* or *meta* substituents because of the effect of steric hindrance (entries 1–6). Note that the reaction of aliphatic aldehyde, such as 2-methyl-propanal, also failed (entry 14).

Table 1 Optimization of this one-pot reaction[a]




1 2 3 4g

| Entry | Base/equiv. | Time/*T* | Yield of **4g**[b] (%) |
|---|---|---|---|
| 1 | —[c] | 24/reflux | 0 |
| 2 | $Et_3N$/0.25 | 12/r.t. | 60 |
| 3 | $Et_3N$/0.25 | 12/reflux | Trace |
| 4 | Pyridine/0.25 | 12/r.t. | 30 |
| 5 | Pyridine/0.25 | 12/reflux | 0 |
| 6 | Piperidine/0.25 | 12/r.t. | Trace |
| 7 | Piperidine/0.25 | 12/reflux | Trace |
| 8 | $NH_4OAc$/0.5 | 12/r.t. | 0 |
| 9 | $NH_4OAc$/0.5 | 12/reflux | 0 |
| 10 | L-Proline/0.25 | 12/r.t. | 0 |
| 11 | L-Proline/0.25 | 12/reflux | 0 |
| 12 | $Et_3N$/0.5 | 12/r.t. | 72 |
| 13 | $Et_3N$/1 | 12/r.t. | 72 |
| 14 | $Et_3N$/10 | 12/r.t. | 72 |
| 15 | $Et_3N$/0.5 | 24/r.t. | 72 |

[a] Reaction conditions: **1** (1.0 mmol), **2g** (2.0 mmol), **3** (1.0 mmol), solvent: DMSO, 6 mL. [b] Isolated yield. [c] In the absence of base.

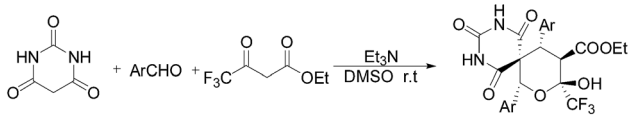
The structures of the compounds **4(a–k)** were fully confirmed by $^1H$, $^{19}F$, and $^{13}C$ NMR spectroscopy, mass spectrometry, high-resolution mass spectrometry and IR spectroscopy. For instance, among the characteristic features of the $^1H$ NMR spectrum of **4g** in $CDCl_3$, doublets appeared at $\delta = 4.40$ and 4.56 ppm with a coupling constant of $J_{H-H} = 13.0$ Hz for H-10 and H-11 protons, respectively, indicating a *trans* configuration of the vicinal pair of hydrogen atoms. The stereochemistry of **4** was attributed to intra-molecular cyclization being an energetically favorable process, affording the more stable '*trans*' configuration of **4**. For the same reason, the stereochemistry of carbons C-7 and C-11 were *R** and *S**, respectively. In the $^{19}F$ NMR spectrum, the trifluoromethyl group appeared as a singlet peak at $\delta = -85.14$ ppm (s, 3F), which indicated that this group was bonded to a quaternary carbon atom. The structure of compound **4d** was further confirmed by single crystal X-ray analysis, which supported our speculations regarding the structures of the products (Fig. 1).[22]

On the basis of our results, we propose a plausible mechanism for the formation of compounds **4** (Scheme 1). First, one molecule of barbituric acid condensed with one molecule of aromatic aldehyde *via* an initial Knoevenagel condensation reaction, then followed by a Michael addition reaction catalyzed by $Et_3N$, thus, the intermediate **A** was formed. Intermediate **A** reacted with the second molecule of aromatic aldehyde to afford the intermediate **B**, which underwent the intramolecular cyclization reaction to afford the products **4** eventually.

Furthermore, we studied the dehydration of compound **4**. It should be indicated that the hemi-ketal moiety in compound **4** is stable and resists dehydration under the conditions for formation of **4** because of the strong electron-withdrawing effect of the trifluoromethyl group on the six-membered ring.[23] Thus, the effect of different dehydrated reagents was briefly screened, and reaction results showed that the excess of 4-toluenesulfonic acid or phosphorus pentoxide were not effective even though the reaction was performed under reflux in toluene. It was found that the treatment of **4** with an excess of $SOCl_2$/pyridine in $CH_3CN$ at room temperature caused the smooth elimination of water from **4** to afford the corresponding dehydrated derivatives **5**. The reaction results are listed in Table 3. The structure of compound **5** was fully supported by appropriate methods.

Table 2 Results of the one-pot, three component reaction[a]




1 2 3 4

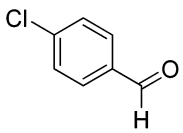
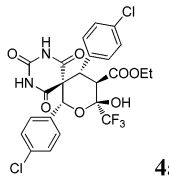
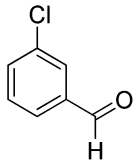
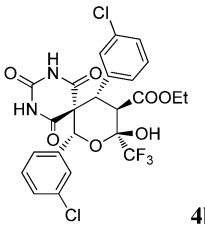
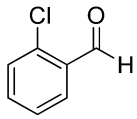
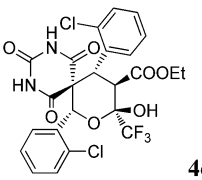
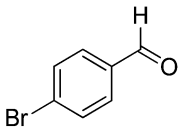
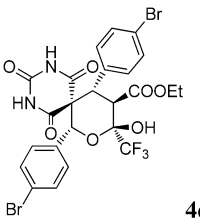
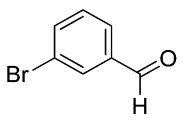
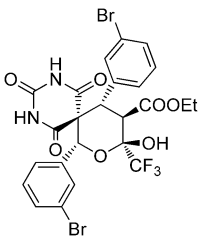
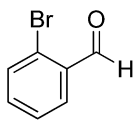
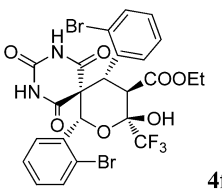
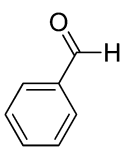
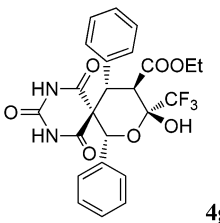
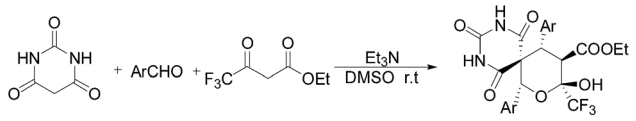
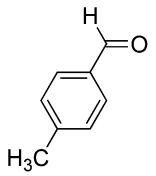
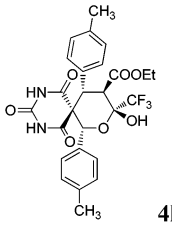
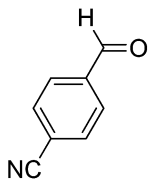
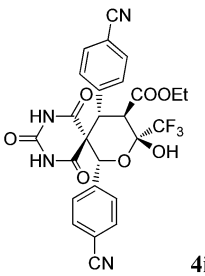
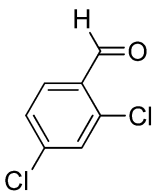
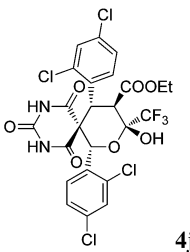
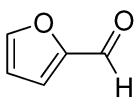
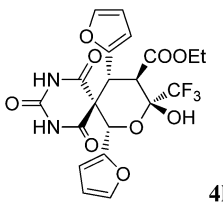
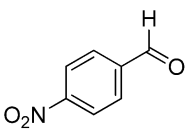
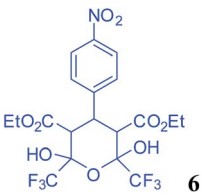
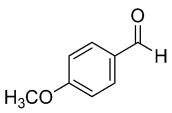
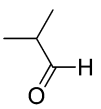
| Entry | Ar | Time/h | Products | Yield[b] (%) |
|---|---|---|---|---|
| 1 |  | 24 |  **4a** | 78 |
| 2 |  | 24 |  **4b** | 73 |
| 3 |  | 12 |  **4c** | 63 |
| 4 |  | 12 |  **4d** | 82 |
| 5 |  | 8 |  | 72 |
| 6 |  | 12 |  **4f** | 65 |
| 7 |  | 24 |  **4g** | 72 |

Table 2 (*Contd.*)




1 2 3 4

| Entry | Ar | Time/h | Products | Yield[b] (%) |
|---|---|---|---|---|
| **8** |  | 12 |  **4h** | 71 |
| **9** |  | 12 |  **4i** | 76 |
| **10** |  | 12 |  **4j** | 74 |
| **11** |  | 24 |  **4k** | 76 |
| **12** |  | 12 |  **6** | 68[c] |
| **13** |  | 12 | — | — |
| **14** |  | 24 | — | — |

[a] Reaction conditions: **1** (1.0 mmol), **2** (2.0 mmol), **3** (1.0 mmol), $Et_3N$ (0.5 eq.), DMSO (6.0 mL), room temperature. [b] Isolated yield. [c] Yield is calculated based on ethyl-4,4,4-trifluoro-3-oxobutanoate.

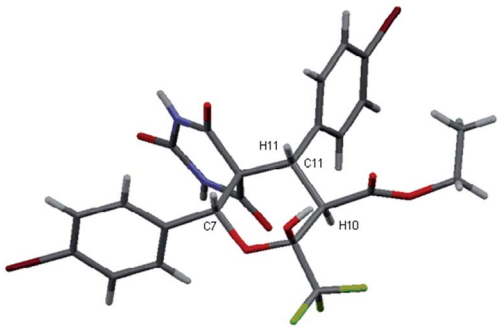
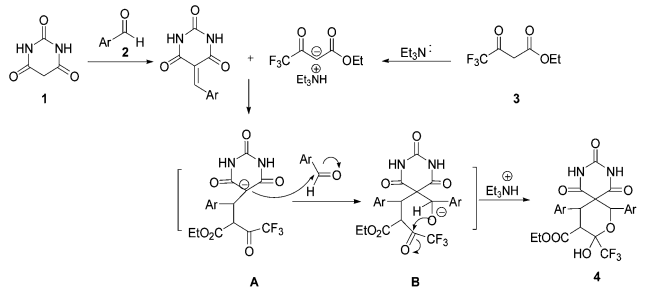


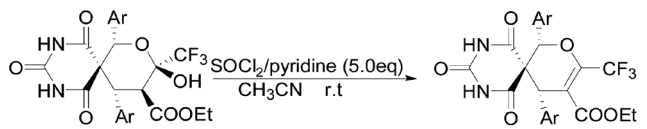

Fig. 1 X-ray crystal structure of compound **4d**.




Scheme 1 Plausible mechanism for formation of **4**.

From the step-economical reaction point of view, we finally developed a step-wise cycloaddition-dehydration reaction into a one-pot strategy. The reaction mixture **4g** was allowed to react with an excess of thionyl chloride (5.0 eq.) and pyridine (5.0 eq.) after cycloaddition was finished. By a combination of cycloaddition and dehydration sequences, this one-pot reaction gave the final product **5d** in comparable yields (55%, compared to 37% under the separated step reaction). During this process, the structure of **5a** was also confirmed by spectral data.

Table 3 Reaction results of dehydration of **4** to **5**[a]




| Entry | Ar | Time/h | Products[b] (Yield/%) |
|---|---|---|---|
| 1 | *p*-$ClC_6H_4$ | 2 | **5a** (59) |
| 2 | *m*-$BrC_6H_4$ | 2 | **5b** (50) |
| 3 | *o*-$ClC_6H_4$ | 2 | **5c** (63) |
| 4 | $C_6H_5$ | 2 | **5d** (51) |
| 5 | 2,4-$(Cl)_2C_6H_3$ | 2 | **5e** (50) |
| 6 | *p*-$CH_3C_6H_4$ | 2 | **5f** (52) |
| 7 | Furyl-2- | 2 | **5g** (58) |

[a] Reactions were performed with **4** (1.0 mmol), $SOCl_2$ (5.0 mmol) and pyridine (5.0 mmol) in $CH_3CN$ (10 mL). [b] Isolated yield.

## Conclusions

In conclusion, we demonstrated a simple and convenient multi-component protocol for the synthesis of a library of ethyl 7,11-diaryl-9-hydroxy-1,3,5-trioxo-9-(trifluoromethyl)-8-oxa-2,4-diazaspiro[5.5]undecane-10-carboxylate derivatives from readily available simple starting materials. Dehydration of the hemiketal moiety to form the corresponding ethyl-7,11-diaryl-1,3,5-trioxo-9-(trifluoromethyl)-8-oxa-2,4-diazaspiro[5.5]undec-9-ene-10-carboxylate derivatives was also achieved. Furthermore, the step-wise cycloaddition and dehydration reactions can be further developed into a one-pot strategy with enhanced yields. These novel compounds can be considered as useful trifluoromethyl-containing substrates for the synthesis of a variety of heterocyclic compounds with potential biological activities in the biomedical field.

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