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Synthesis of 1,1,1-trihalo-4-methoxy-4-[2-heteroaryl]-3-buten-2-ones, the corresponding butan-1,3-dione and azole derivatives

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Abstract—The synthesis of 1,1,1-trihalo-4-methoxy-4-[2-thienyl]-3-buten-2-ones, 1,1,1-trihalo-4-methoxy-4-[2-furyl]-3-buten-2-ones and the respective trihalomethyl 1,3-butanone derivatives by trihaloacylation of dimethoxy acetals derived from 2-acetylthiophene and 2-acetylfuran are reported. This is a convenient method to obtain fluorinated and chlorinated 1,3-dielectrophiles from 2-acetylthiophene and 2-acetylfuran. The fluorinated 1,3-dielectrophiles were used to synthesize five new 2-thienyl- and 2-furylazoles. The structure of all products were assigned by ^{1}HH- and ^{13}C NMR and mass spectrometry. © 2002 Elsevier Science Ltd. All rights reserved.

The introduction of a trifluoromethyl or trichloromethyl groups into an organic compound can bring about remarkable changes in the physical, chemical and biological proprieties that result in new compounds or materials suitable for diverse pharmacological,[1] agrochemical,[2] analytical[3] and synthetic applications.[4]

On the other hand, the most employed method to obtain trifluoromethyl β-diketones is via acylation of enolates with perfluoroalkanoates.[5] The perfluorinated esters are commercially available and they are usually obtained by esterification of the respective perfluorinated acids, which is not an explicit reported method. Strong bases such as sodium methoxide and sodium amide are used to obtain enolates from ketones and the overall yields for the enolate formation and subsequent acylation are only moderate. The majority of methods found in the literature referring to the synthesis of 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanodione[5] relies on the Park's work[6] (Claisen condensation). We found only one reference about trichloromethyl β-diketones in the literature.[7] The lack of literature data is probably because the acylation of enolates by the ester method is of limited use to obtain perchloroalkyl β-diketones, due to the lability of the perchloroalkyl groups in basic medium.[8]

The haloacetylation of acyclic enol ethers and acetals, described elsewhere,[7] affords 1,1,1-trihalo-4-alkoxy-3-alken-2-ones which have been used as precursors for heterocycles and acyclic compounds.[9] In general, the presence of a trihalomethyl group in the precursor is a determining factor to establish the regiochemistry of the heterocyclic ring. The transformation of the trichloromethyl group, under mild conditions, into carboxylic groups led us to devote special attention to these substrates.[10] Despite extensive studies on the applications of 1,1,1-trihalo-4-alkoxy-3-alken-2-ones in heterocyclic chemistry, the strategy to synthesize heteroaryl substituted 1,1,1-trihalo-4-methoxy-3-alken-2-ones and their usefulness to the synthesis of heterocycles has not yet been developed. These compounds are highly functionalized intermediates which may be useful for further synthetic applications.

In this paper, we report a new and efficient synthetic approach for the synthesis of a series 1,1,1-trihalo-4-methoxy-4-[2-thienyl]- (**1a**, **2a**) and 4-[2-furyl]-3-buten-2-ones (**1b**, **2b**) and the respective 4,4,4-trihalo-1-[2-heteroaryl]-1,3-butanediones derivatives (**3a**,**b**, **4a**,**b**) We show that trifluoromethyl substituted 1,3-dielectrophiles (**1**, **3**) react with hydroxylamine and hydrazine leading to a new series of biheterocycles 2-thienyl- and 2-furylazoles (**5a**,**b**, **6b**, **7a**,**b**) (Scheme 2).

The dimethoxy acetals derived from 2-acetylthiophene and 2-acetylfuran were obtained from the reaction of these ketones and trimethyl orthoformate in the pres-

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ence of *p*-toluenesulfonic acid.[11] The trihaloacylation reactions were carried out in chloroform or dichloromethane and pyridine at −10 to 30°C for 8–12 h. Two equivalents of acylating agent per acetal was required to obtain the 1,1,1-trihalo-4-methoxy-4-[2-heteroaryl]-3-buten-2-ones (**1**, **2**) since one molecule of the acylant promotes the formation of the enol ether by trapping the alkoxy group liberated by the acetal and the second molecule of the acylant promotes the acylation.[12] The acylation products obtained without hydrolysis furnished black oil mixtures of the (*E*/*Z*)-1,1,1-trihalo-4-methoxy-4-[2-heteroaryl]-3-buten-2-ones (**1**, **2**) and the respective 4,4,4-trihalo-1-[2-heteroaryl]butan-1,3-dione (**3**, **4**) with variable ratios (Scheme 1). The *E*-configuration isomer was the major compound in all mixtures. The configuration of isomers was assigned on the basis of $^{3}J_{C2'-H3}$ coupling constants.[13]

The acylated products obtained from the hydrolysis path furnished only 4,4,4-trihalo-1-[2-hetaryl]butan-1,3-diones **3a**,**b**,[14] **4a**,**b** in high purity (Scheme 1). For the 1,3-dicarbonyl compounds **3a**,**b**,[14] **4a**,**b** isolated from the hydrolysis path, was observed only one set of ^{1}H and ^{13}C NMR signals which indicates that only one enolic form was obtained for each compound. ^{1}H NMR spectra showed the signal for the enolic hydrogen within 12–15 ppm for all compounds and the chemical shifts for H2 and C2 in the range of 6.4–6.7 and 89–83.5 ppm, respectively (Table 1).

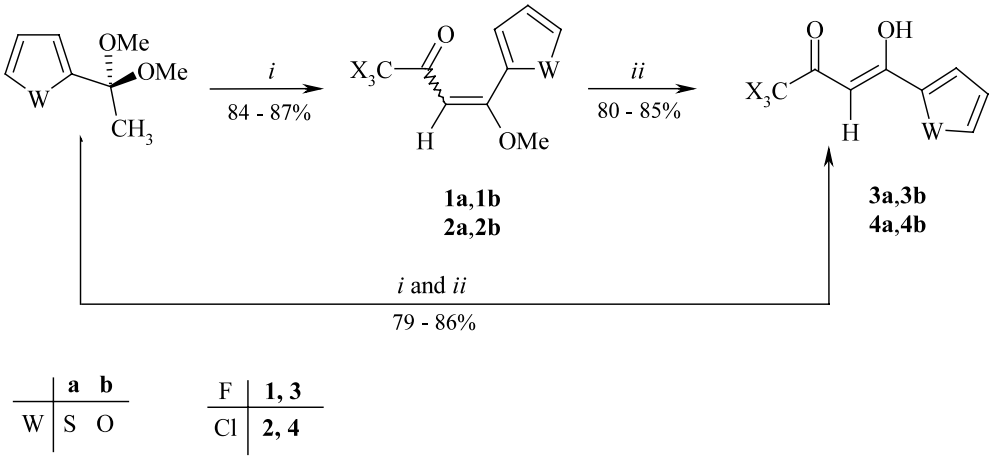
The cyclization of compounds **1a**,**b** (*E*/*Z*) or **3a**,**b** with hydroxylamine hydrochloride was carried out in the presence of pyridine in a molar ratio of 1.0:1.2:1.2, respectively, and the mixture was stirred at 50°C for 8 h to afford a new series of 3-[2-heteroaryl]-5-trifluoromethyl-4,5-dihydroisoxazoles **5a** or **5b** in 95% yield. Compounds **1a**,**b** and **3a**,**b** also reacted with dry hydrazine to furnish 3(5)-trifluormethyl-5(3)-(2-thienyl)pyrazole **6a**[15] or 3(5)-trifluoromethyl-5(3)-(2-furyl)pyrazole **6b**.

The reaction of **3a**,**b** with thiosemicarbazide hydrochloride led to a new series of 5-trifluoromethyl-5-hydroxy-3 - [2 - heteroaryl] - 1*H* - 1 - pyrazolethiocarboxy amides (**7a**,**b**) (Scheme 2).

Unless otherwise indicated all common reagents and solvents were used as obtained from commercial suppliers without further purification. All melting points were measured using a Reichert–Thermovar melting-point microscope and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 400 (^{1}H at 400.13 MHz and ^{13}C at 100.62 MHz), 5 mm sample tubes, 300 K, digital resolution ±0.01 ppm, in $CDCl_3$/TMS. Mass spectra were recorded using an HP 5973 MSD connected to an HP 6890 GC and interfaced by a Pentium PC. The GC was equipped with a split–splitless injector, autosampler, cross-linked HP-5 capillary column (30 m, 0.32 mm of internal diameter), and helium was used as the carrier gas.

*4,4,4-Trihalo-1-[2-heteroaryl]-1,3-butanediones **3a**,**b**, and **4a**,**b**: general procedure*

To a stirred solution of dimethoxy acetal derived from 2-acetylthiophene or 2-acetylfuran (30 mmol) and pyridine (60 mmol, 4.8 g) in chloroform (30 ml) kept at 0°C, a solution of trichloroacetyl chloride or trifluoroacetic anhydride (60 mmol) in chloroform (20 ml) was added dropwise at −10°C. The mixture was stirred for 8–12 h at room temperature (25–35°C). The mixture was quenched with a 2 M sulfuric acid solution (30 ml) and stirred for 2 h at 50°C. The organic layer was dried with sodium sulfate, the solvent was evaporated and the products were obtained in high purity (see Table 1).



Scheme 1. *Reagents and conditions*: (i) $(F_3CCO)_2O$ or Cl_3CCOCl, pyridine, $CHCl_3$, −10 to 0°C (4 h), 0–30°C (8 h); (ii) H_2SO_4 1 M, 50°C, 5 h.

Table 1. Yields and selected physical and NMR[a] data for 1,1,1-trihalo-4-methoxy-4-[2-thienyl]-3-buten-2-ones (**1a**,**b**) and 1,1,1-trihalo-4-methoxy-4-[2-furyl]-3-buten-2-ones (**1b**, **2b**) and buten-1,3-dione derivatives **3a**,**b** and **4a**,**b**

Compd	M.F.,[b] M.W.	Yield (%)[c]	Ratio[d] $E/Z/\beta$d	GC–MS m/z (%)	^{1}H NMR δ (ppm)[e]	^{13}C NMR δ (ppm) [J_{CF} Hz][e]
1a	$C_9H_7F_3O_2S$, 236.21	84	5: 1: 1	236 M^+ (10), 201 (100), 173 (30)	3.95 (3H, OMe), 6.2 (H3); Tn: 7.12 (H4), 7.57 (H3), 8.28 (H5)	117.7 [278] (C1), 178.2 [36.5](C2), 89.6 [2.5] (C3), 168.6 (C4), 56.9 (OMe), Tn: 134.9 (C2), 131.5 (C3), 127.3 (C4), 133.8 (C5)
1b	$C_9H_7F_3O_3$, 220.15	83	10: 1: 1	221 M^+ (30), 204 (30), 153 (70), 69 (100)	4.1 (3H, OMe), 6.7 (H3); Fu: 6.7 (H4), 7.1 (H3), 7.65 (H5)	117.5 [280] (C1), 183 [37] (C2), 89.3 [2.4] (C3), 170 (C4), 56.4 (OMe), Fu: 149 (C2), 113.5 (C3), 114.2 (C4), 146.8 (C5)
2a	$C_9H_7Cl_3O_2S$, 285.58	89	4: 1: 4	285 M^+ (10), 251 (20), 207 (15), 153 (100)	3.95 (3H, OMe), 5.8 (H3); Tn: 7.13 (H4), 7.6 (H3), 8.5 (H5)	98.2 (C1), 176.2 (C2), 90.0 (C3), 169.2 (C4), 56.9 (OMe), Tn: 135.0 (C2), 132.3 (C3), 127.4 (C4), 134.3 (C5)
2b	$C_9H_7Cl_3O_3$, 269.51	87	7: 1: 3	269 M^+ (10), 235 (20), 191 (30), 137 (100)	4.0 (3H, OMe), 6.73 (H3); Fu: 6.6 (H4), 7.27 (H3), 7.65 (H5)	94.7 (C1), 185.5 (C2), 88.8 (C3), 170.5 (C4), 55.7 (OMe), Fu: 147.9 (C2), 113.1 (C3), 114.1 (C4), 147.2 (C5)
3a	$C_8H_5F_3O_2S$, 222.19	82	–	222 M^+ (30), 153 (60), 111 (40), 69 (100)	13.7 (OH), 6.46 (H2); Tn: 7.2 (H4), 7.7 (H3), 7.85 (H5)	182.7 (C1), 93.4 [2.6] (C2), 171 [36.6] (C3), 117.6 [280.2] (C4), Tn: 139.3 (C2), 132.7 (C2), 128.8 (C4), 135.3 (C5)
3b	$C_8H_5F_3O_3$, 206.12	79	–	206 M^+ (80), 178 (10), 137 (100)	14.0 (OH), 6.5 (H2); Fu: 6.64 (H4), 7.35 (H3), 7.7 (H5)	176.7 (C1), 92.7 [2.4] (C2), 173.5 [36.7] (C3), 118 [281] (C4); Fu: 148.9 (C2), 118.7 (C3), 113.3 (C4), 147.9 (C5)
4a	$C_8H_5Cl_3O_2S$, 271.54	86	–	272 M^+ (25), 207 (30), 153 (100)	13.7 (OH), 6.7 (H2); Tn: 7.2 (H4), 7.7 (H3), 7.85 (H5)	184.3 (C1), 89.3 (C2), 176.5 (C3), 94.5 (C4), Tn: 137.2 (C2), 131.5 (C3), 128.7 (C4), 133.6 (C5)
4b	$C_8H_5Cl_3O_3$, 255.48	85	–	256 M^+ (10), 191 (25), 137 (100)	13.8 (OH), 6.7 (H2); Fu: 6.25 (H4), 7.25 (H3), 7.65 (H5)	185.4 (C1), 88.7 (C2), 170.4 (C3), 94.6 (C4), Fu: 147.8 (C2), 117.1 (C3), 113.1 (C4), 147.2 (C5)

[a] NMR spectra were recorded on a Bruker DPX 400 (^{1}H at 400.13 MHz and ^{13}C at 100.61 MHz) in $CDCl_3$/TMS. Of the four β-diketones whose NMR spectroscopy is described here for the first time.
[b] Satisfactory elemental analysis performed on a Vario EL Foss Heraeus apparatus (C±0.4%; H±0.6)
[c] Yields of isolated mixtures for **1** (*E*,*Z*) and **2** (*E*,*Z*) and pure diketones **3** and **4**.
[d] Ratio determined by GC and ^{1}H NMR integrals.
[e] Data for *E* isomers of **1** and **2**.

*Synthesis of 3-[2-heteroaryl]-5-trifluoromethyl-4,5-dihydroisoxazoles (**5a**,**b**)*

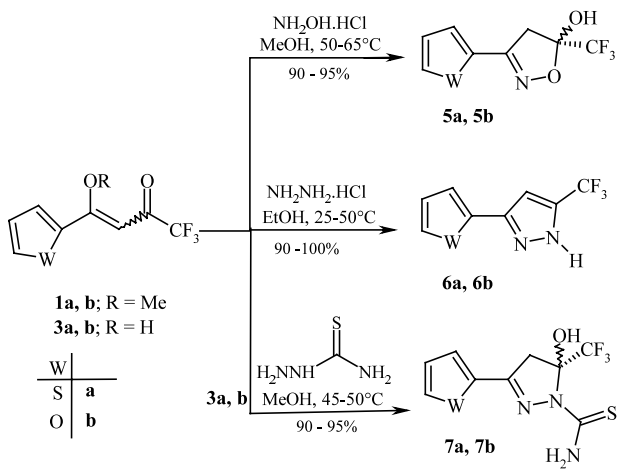
To a solution of 4,4,4-trifluoro-1-[2-heteroaryl]-1,3-butanedione (**3a**,**b**) (5 mmol) in pyridine (0.52 g, 6.5 mmol) and methanol (5 ml) was added hydroxylamine hydrochloride (0.45 g, 6.5 mmol). The mixture was stirred for 8 h at 50°C. The solvent was evaporated and the solid residue was washed with water and dried under vacuum. Isoxazole compounds were fully characterized by spectroscopic methods. Data for **5a**: $C_8H_6F_3NO_2S$; mp 119–123°C; ^{1}H NMR: Isox δ 3.6 (H4), 4.0 (H4), Thienyl δ 7.7 (H5), 7.5 (H3), 7.2 (H4); ^{13}C NMR: δ Isox 153.0 (C3), 42.8 (C4), 103.7 (C5, $J_{CF}=33$ Hz), 122.4 (CF_3, $J_{CF}=284$ Hz). Anal. calcd: C, 40.51; H, 2.55; N, 5.90. Found: C, 40.6; H, 2.7; N, 6.0%. Data for **5b**: $C_8H_6F_3NO_3$; mp 117–120°C; ^{1}H NMR: Isox δ 3.5 (H4), 3.8 (H4), Furyl δ 7.7 (H5), 6.9 (H3), 6.6 (H4); ^{13}C NMR: δ Isox 148.7 (C3), 42.5 (C4), 103.6 (C5, $J_{CF}=33.6$ Hz), 122.6 (CF_3, $J_{CF}=282$ Hz). Anal. calcd: C, 43.45; H, 2.73; N, 6.33. Found: C, 43.6; H, 2.7; N, 6.5%.

*Synthesis of 3(5)-[2-heteroaryl]-5(3)-trifluoromethyl-1H-pyrazoles (**6a**,**b**)*

A solution of 4,4,4-trifluor-1-[2-heteroaryl]-1,3-butanedione (**3a**,**b**) (5 mmol) in chloroform (5 ml) was added dropwise to a cooled stirred solution (−10°C) of dry hydrazine (0.2 g, 5.5 mmol). The mixture was stirred for 1 h and the solvent was evaporated. The solid residue was washed with water and dried under vacuum. Pyrazole compounds were fully characterized by spectroscopic methods. Data for **6a**: $C_8H_5F_3N_2S$ (lit. 15); ^{1}H NMR: Pyz δ 6.65 (H4), Thienyl δ 7.35 (H5), 7.0 (H4), 7.3 (H3); ^{13}C NMR: δ Pyz 143.7 (C3), 101.5 (C4, $J_{CF}=1.6$ Hz), 143.0 (C5, $J_{CF}=38.4$ Hz), 122.4 (CF_3, $J_{CF}=269$ Hz). Data for **6b**: $C_8H_5F_3N_2O$; mp 41–43°C; ^{1}H NMR: Pyz δ (H4), Furyl δ 7.7 (H5), 6.9 (H3), 6.6 (H4); ^{13}C NMR: δ Isox 148.7 (C3), 42.5 (C4), 103.6 (C5, $J_{CF}=33.6$ Hz), 122.6 (CF_3, $J_{CF}=282$ Hz). Anal. calcd: C, 47.54; H, 2.49; N, 13.86. Found: C, 47.6; H, 2.5; N, 13.7%.

*Synthesis of 3-[2-heteroaryl]-5-trifluoromethyl-4,5-dihydro-1H-1-pyrazolethiocarboxyamides (**7a**,**b**)*

A solution of 4,4,4-trifluor-1-[2-hetaryl]-1,3-butanedione (**3a**,**b**) (5 mmol) and thiosemicarbazide (0.45, 5 mmol) in methanol (10 ml) was stirred overnight at 25–30°C. The solvent was evaporated and the solid residue was washed with water and dried under vacuum. Pyrazolethiocarboxyamides were fully characterized by spectroscopic methods. Data for **7a**: $C_9H_8F_3N_3OS_2$; mp 99–102°C; ^{1}H NMR: Pyz δ 3.65 (H4), 3.85 (H4), Thienyl δ 7.54 (H5), 7.12 (H4), 7.3 (H3); ^{13}C NMR: δ Pyz 148.6 (C3), 45.0 (C4), 92.8 (C5, $J_{CF}=34$ Hz), 125.3 (CF_3, $J_{CF}=282$ Hz). Anal. calcd: C, 36.61; H, 2.73; N, 14.23. Found: C, 36.5; H, 2.7; N, 14.4%. Data for **7b**: $C_9H_8F_3N_3O_2S$; mp 95–98°C; ^{1}H NMR: Pyz δ 3.7 (H4), 3.91 (H4), Furyl δ 7.8 (H5), 7.1 (H3), 6.6 (H4); ^{13}C NMR: δ Pyz 145.8 (C3), 43.3 (C4), 93.4 (C5, $J_{CF}=34$ Hz), 124.6 (CF_3, $J_{CF}=282$ Hz). Anal. calcd: C, 38.71; H, 2.89; N, 15.05. Found: C, 38.8; H, 2.9; N, 15.2%.



Scheme 2.

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