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Detrifluoroacetylation of 4,4,4-trifluoro-3,3-dihydroxy-2-(hydroxyimino)butan-1-ones as a convenient synthetic strategy for acyl cyanides

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ABSTRACT

A reaction reinvestigation of fluorinated 1,3-dicarbonyl compounds with $NaNO_2$ in acidic conditions revealed the formation of corresponding 1,1,1-trifluoro-3-hydroxyimino-butan-2,4-diones which predominantly isolated as hydrates. A novel synthesis of ethoxy-, alkyl-, (het)aryl substituted carbonylcyanides via acid-catalyzed detrifluoroacetylation of obtained 2-hydroxyimino derivatives of 1,3-dicarbonyl compounds was described.

1. Introduction

Trifluoroacetyl group is one of widely used functionalities in organic synthesis and plays a significant role in the construction of fluorinated building blocks, such as enones, 1,3-diketones, heterocyclic derivatives [1]. The electron-withdrawing properties of CF_3 group enhanced the electrophilicity of carbonyl carbon atom thereby promoting the nucleophilic attack by different *N,O,C*-reagents [2]. In contrast to nonfluorinated analogs, the ability of the trifluoromethyl group to stabilize acetals, hydrates or aminals is well known for trifluoroacetyl derivatives [3].

The loss of the $CF_3C(O)$ moiety is usually an unexpected result which is rarely reported in the literature [1b,4]. Recently, much attention has been devoted to detrifluoroacetylation approaches of some 1,1,1-trifluoro-2,4-dione derivatives. Applications of this methodology as a convenient route to *in situ* difluoro(fluoro) enolate generation for reactions with different electrophiles have been reviewed [1b] (Fig. 1). The elimination of the trifluoroacetyl group after functionalization of 1,1,1-trifluoro-2,4-diones has been used in the synthesis of hardly available α,β-unsaturated ketones [4a], γ-nitroketones [4b], α-diazoketones [4c], N-substituted α-amino esters and α-aminoketones [4d]. The base or nucleophile action on the trifluoroacetyl derivatives resulting in $CF_3C(O)$ group elimination is one of the main features in most cases thus far studied.

Among fluorinated 2-functionalized 1,3-dicarbonyl compounds, 2-hydroxyimino derivatives **2** are less studied (Fig. 1) [5]. To the best of our knowledge, only a few reports have been described applications of such derivatives in pyrazoles, [5b–f] benzodiazepines [5e,f] and aminoacids [5g] preparation. In most cases hydroxyimino derivatives **2** have been used without isolation as *in situ* prepared intermediates. From this point, their applications are still limited. It has been mentioned, that some of **2** could not be isolated from the reaction mixture probably due to their low stability [5a,f]. For almost two last decades, only two examples of trifluorinated hydroxyimino derivatives **2** were characterized by IR and ^1H NMR spectra [5f,g].

Hence, our motivation in this work was to explore the peculiarities of trifluorinated 2-hydroxyimino-1,3-dicarbonyl compound preparation and their isolation in pure form, which would provide the opportunities for broad investigation of their properties and applications. Herein, we wish to report on acid-catalyzed detrifluoroacetylation of 4,4,4-trifluoro-3,3-dihydroxy-2-(hydroxyimino)butan-1-ones to yield carbonylcyanides under mild conditions.

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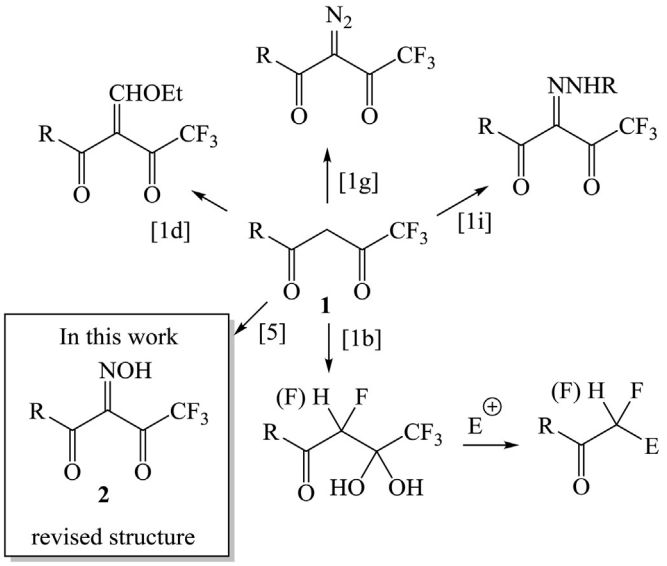


Fig. 1. The examples of 3-functionalized 1,1,1-trifluorobutan-2,4-diones.

2. Results and discussion

We commenced our study with the nitrozation of trifluorinated 1,3-diketones **1a–k** with $NaNO_2$ in aqueous AcOH accordingly to our previous study. In contrast to non-fluorinated analogs the formation of hydrates **3a–h** of expected 2-hydroxyimino-1,3-diketones **2** was observed (checked by reaction mixture ^{19}F NMR spectra monitoring) (Scheme 1). In case of trifluoroacetoacetone hydrate **3k** was identified by ^{19}F NMR spectra of reaction mixture but all attempts of the product **3k** isolation were failed.

The products **3a–h** are white solids, insoluble in chloroform, stable at store for months at ambient conditions. However, to achieve a complete removal of solvent under products **3g,h** isolation the vacuum evaporation on a water bath at 60 °C was required. It resulted in a partial dehydration of obtained products **3g,h** and formation of a mixture containing diketo form **2g,h** in addition to target compounds **3g,h** (see Table 1).

It should be mentioned that the traces of acetic acid in isolated products were identified even after several neutralization steps. Acidic impurities can result in by-products formation under the further transformations of **3** as starting compounds. For example, in case of the gram scale preparation of **3**, GC–MS analysis of the reaction mixture revealed the formation of non-fluorinated by-products (5–10%) as acyl nitriles and their derivatives. To facilitate the product **3** purification and avoid detrifluoroacetylation process caused by acetic acid we attempted to apply acid with low solubility in organic media.

The use of citric acid (2 equiv) in the reaction of 1,3-dicarbonyl compounds (1 equiv) with $NaNO_2$ (1.2 equiv) allowed us to avoid neutralization step due to the high solubility of this organic acid in water. As a result, the yields of isolated products have increased and reaction wastes reduced (Table 1). It should be noted that detrifluoroacetylative products were not observed in the reaction mixtures under such conditions (according to GC–MS analysis). The developed synthesis is reproducible and scalable to allow the target compounds to be easily prepared in gram quantities (up to 5 g of compounds at one synthesis run).

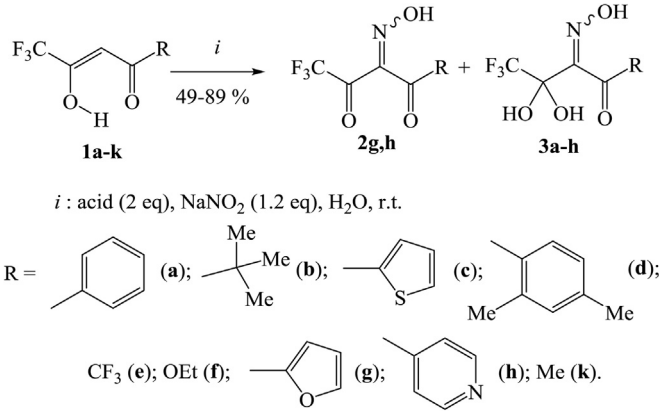
The NMR spectra of obtained compounds confirmed that these products exist predominantly as 4,4,4-trifluoro-3,3-dihydroxy-2-(hydroxyimino)butan-1-ones (**3a–h**). A characteristic feature of their ^1H NMR spectra (DMSO-d_6) is the appearance of the 2 singlets at δ 11.70–12.08 and 6.4–7.78 ppm for NOH and $CF_3C(OH)_2$ protons, respectively. In the ^{19}F NMR spectra of **3a–h** the signal of CF_3 group attached to the sp^3-hybridized carbon atom is exhibited as the singlet at δ_F from −82.7 to −81.7 ppm. In the ^{13}C NMR spectra of **3a–h** the CF_3-*C* was identified by spin-spin coupling constant $^2J_{CF} \sim 37$ Hz. This quartet is appeared at $\delta_C \sim 92$ ppm. The signals of diketo form (**2g,h**) in NMR spectra are up-shielded in contrast to that of hydrate forms (**3g,h**). Dehydrated form **2g,h** has been easily identified by the presence of signals at δ_F from −71.6 to −71.5 ppm in the ^{19}F NMR spectra.

Next, we focused on the preparation of acyl cyanides **4** from obtained hydroxyimino derivatives **3**. We found that the reaction of compounds **3a–h** with acetic anhydride in $CHCl_3$ under reflux gave corresponding carbonylcyanides **4a–d,f–h** in moderate yields (Table 2,Scheme 2). For compound **3e** only the mixture of decomposition products was obtained. This reaction proceeded with clear solution formation after heating of the starting suspension for 10–15 min. Further product isolation by column chromatography or distillation was required because of by-products formation derived from reactive acyl cyanides **4a–d,f–h** (checked by GC–MS analysis and ^1H NMR data). We also found that the acetic acid action on compounds **3a-h** resulted in acyl cyanides **4a–d,f–h** in good yields.

It is important to note that this simple procedure represents a convenient synthetic approach to acyl nitriles that are versatile multifunctional intermediates [6]. The classical methods of acyl cyanides synthesis usually require the metal cyanides use at a high reaction temperature while the alternative ways mostly involve the several steps, including cyanosilylation, cyanohydrin formation, and oxidation [7]. However, the process described here does not require the use of hazardous chemicals or harsh reaction conditions. Furthermore, the detrifluoroacetylation occurs in the absence of common bases that are usually employed for the trifluoroacetic group elimination.

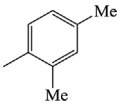
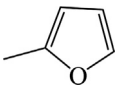
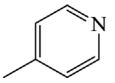
We can assume that the proposed mechanism is realized via either acylation or protonation of hydroxyimino moiety of **3** with the formation of intermediates **A** or **B** respectively (Scheme 2). It should be noted that acylation of non-fluorinated 2-hydroxyimino analogs of **2** proceeds smoothly under the same conditions [8]. In case of compounds **3**, the formation of **A** or **B** resulted in the elimination of trifluoroacetic and acetic acids to yield compounds **4**.

In conclusion, a practical approach for 2-hydroxyimino derivatives of trifluorinated 1,3-dicarbonyl compounds was elaborated. Detrifluoroacetylation of products obtained was demonstrated to be an acid-catalyzed process. Another possible



Scheme 1. The nitrozation of trifluorinated 1,3-diketones.

Table 1
Scope of 4,4,4-trifluoro-3,3-dihydroxy-2-(hydroxyimino)butan-1-ones **3**.

Entry	Dicarbonyl compound	R	Reaction conditions[a]	Yield[b], %	Ratio of 3:2	Mp, °C
1	**1a**		AcOH/H_2O Citric acid/H_2O	55 84	100:0 100:0	83–84
2	**1b**		AcOH/H_2O Citric acid/H_2O	49 78	100:0 100:0	86–87
3	**1c**		AcOH/H_2O Citric acid/H_2O	52 87	100:0 100:0	87–88
4	**1d**		AcOH/H_2O Citric acid/H_2O	51 85	100:0 100:0	90–91
5	**1e**	CF_3	Citric acid/H_2O	71	100:0	30–31
6	**1f**	OEt	Citric acid/H_2O	78	100:0	32–33
7	**1g**		Citric acid/H_2O	84[c]	10:6	149–150
8	**1h**		Citric acid/H_2O	89[c]	20:7	180–181
9	**1k**	Me	AcOH/H_2O Citric acid/H_2O	0 0		

[a] Reaction conditions: dicarbonyl compound **1a–k** (30 mmol), $NaNO_2$ (2.48 g, 36 mmol), acid (60 mmol), H_2O (20 ml), r.t.
[b] Yields of isolated products.
[c] Overall yield for a mixture of **2** and **3**.

applications of obtained 2-hydroxyimino derivatives of trifluorinated 1,3-diketones are underway now in our laboratory.

3. Experimental part

All reagents and solvents are commercially available and were used without further purification. The ^1H (500 MHz), ^{19}F (470 MHz), ^{13}C (125 MHz) NMR spectra were recorded on a Bruker AVANCE-500 spectrometer with TMS and C_6F_6 as internal standards. ^{19}F chemical shifts have been reported relative to $CFCl_3$ as an external standard. Melting points were obtained on a Stuart SMP3 apparatus in open capillaries. Reactions were monitored by thin layer chromatography (TLC) with 0.20 mm Alugram Sil G/UV_{254} pre-coated silica gel plates (60 F254). GC–MS analysis was carried out by using Agilent GC 7890A MS 5975C Inert XL EI/CI GC–MS spectrometer with a quadrupole mass-spectrometric detector with electron ionization (70 eV) and scan over the total ionic current in the range m/z = 20–1000 and a quartz capillary column HP-5MS (30 m–0.25 mm, film thickness 0.25 mm).

3.1. General method of the nitrozation of 1,3-dicarbonyl compounds

To a mixture of **1a–k** (20 mmol) and citric acid (40 mmol) in 10 ml of water sodium nitrite 1.65 g (24 mmol) dissolved in 8 ml of water was added. Reaction mixture was stirred for 1 h. Then obtained solution was extracted with Et_2O (2 × 20 ml) and the organic fractions were dried over $MgSO_4$ and concentrated under vacuum to afford hydroxyimino derivatives **3a–h, 2 g**,**h**.

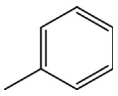
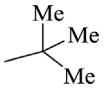
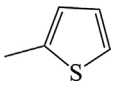
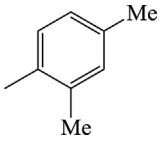
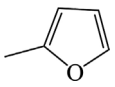
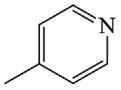
3.2. 4,4,4-Trifluoro-3,3-dihydroxy-2-(hydroxyimino)-1-phenylbutan-1-one (*3a*)

^1H NMR (500 MHz, DMSO-d_6): δ = 7.55 (m, 2H, Ph), 7.66 (m, 1H, Ph), 7.87 (m, 2H, Ph), 7.88 (s, 2H, 2 OH), 11.86 (s, 1H, NOH) ppm. ^{19}F NMR (470 MHz, DMSO-d_6): δ = −81.8 (s, CF_3) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 91.63 (q, CF_3, J = 32 Hz), 122.66 (q, J = 290 Hz), 128.69, 128.98, 133.87, 135.06, 154.18, 192.26 ppm. MS (EI) m/z 244.90 $[M\text{-}H_2O]^+$.

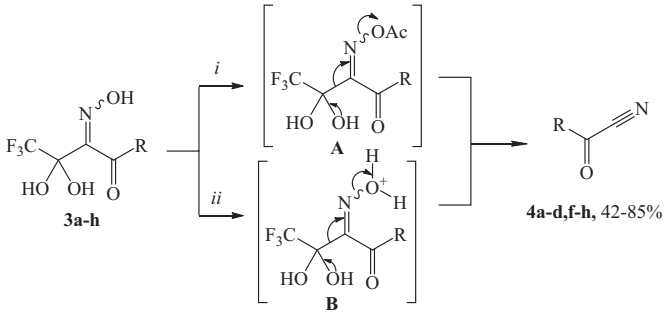
3.3. 6,6,6-Trifluoro-5,5-dihydroxy-4-(hydroxyimino)-2,2-dimethylhexan-3-one (*3b*)

^1H NMR (500 MHz, DMSO-d_6): δ = 1.12 (s, 9H, 3 Me), 7.78 (s, 2H, 2 OH), 11.74 (s, 1H, NOH) ppm. ^{19}F NMR (470 MHz, DMSO-d_6): δ = −81.6 (s, CF_3) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 25.93, 42.27, 91.07 (q, CF_3, J = 34 Hz), 122.67 (q, J = 290 Hz), 155.84, 210.27 ppm. MS (EI) m/z 225.56 $[M\text{-}H_2O]^+$.

Table 2
Scope of carbonylcyanides **4** via detrifluoroacetylation of compounds **3**.

Entry	Starting compound	R	Reaction conditions[a]	Yield of **4**[b], %
1	**3a**		Ac_2O AcOH	85 79
2	**3b**		Ac_2O AcOH	55 44
3	**3c**		Ac_2O AcOH	76 63
4	**3d**		Ac_2O AcOH	81 75
5	**3e**	CF_3	Ac_2O AcOH	0 0
6	**3f**	OEt	Ac_2O AcOH	48 42
7	**3g (+2g)**		Ac_2O AcOH	78 71
8	**3h (+2h)**		Ac_2O AcOH	79 72

[a] Reaction conditions: **3a–h** (20 mmol), acidic reagent (20 mmol), $CHCl_3$, reflux.
[b] Yields of isolated products.



i : Ac_2O (1 eq), $CHCl_3$, reflux; *ii*: AcOH (1 eq), $CHCl_3$, reflux.

Scheme 2. Detrifluoroacetylation of 4,4,4-trifluoro-3,3-dihydroxy-2-(hydroxyimino)butan-1-ones.

*3.4. 4,4,4-Trifluoro-3,3-dihydroxy-2-(hydroxyimino)-1-(thien-2-yl) butan-1-one (**3c**)*

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.28 (m, 1H, Ar), 7.77 (m, 1H, Ar), 7.89 (s, 2H, 2 OH), 8.07 (m, 1H, Ar), 11.95 (s, 1H, NOH) ppm. ^{19}F NMR (470 MHz, DMSO-d_6): δ = −81.9 (s, CF_3) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 91.49 (q, CF_3, *J* = 32 Hz), 122.62 (q, *J* = 288 Hz), 128.80, 135.68, 136.25, 142.48, 153.64, 183.95 ppm. MS (EI) *m/z* 250.87 $[M\text{-}H_2O]^+$.

*3.5. 1-(2,4-Dimethylphenyl)-4,4,4-trifluoro-3,3-dihydroxy-2-(hydroxyimino)butan-1-one (**3d**)*

^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.33 (s, 3H, Me), 2.49 (s, 3H, Me), 7.14 (m, 2H, Ph), 7.66 (m, 1H, Ph), 7.78 (s, 2H, 2 OH), 11.70 (s, 1H, NOH) ppm. ^{19}F NMR (470 MHz, DMSO-d_6): δ = −81.8 (s, CF_3) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 21.01, 21.28, 91.49 (q, CF_3, *J* = 32 Hz), 122.67 (q, *J* = 289 Hz), 126.52, 131.40, 132.40, 132.44, 133.31, 138.92, 142.96, 155.12 ppm. MS (EI) *m/z* 272.94 $[M\text{-}H_2O]^+$.

*3.6. 1,1,1,5,5,5-Hexafluoro-4,4-dihydroxy-3-(hydroxyimino)pentan-2-one (**3e**)*

^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.45 (s, 2H, 2 OH), 12.95 (s, 1H, NOH) ppm. ^{19}F NMR (470 MHz, DMSO-d_6): δ = −82.7 (s, CF_3), −77.2 (s, CF_3) ppm. MS (EI) *m/z* 236.86 $[M\text{-}H_2O]^+$.

*3.7. Ethyl 4,4,4-trifluoro-3,3-dihydroxy-2-(hydroxyimino)butanoate (**3f**)*

^{1}H NMR (500 MHz, DMSO-d_6): δ = 1.22 (t, 3H, Me, *J* = 7 Hz), 4.20 (q, 2H, CH_2, *J* = 7 Hz), 7.85 (s, 2H, 2 OH), 12.08 (s, 1H, NOH) ppm. ^{19}F NMR (470 MHz, DMSO-d_6): δ = −82.3 (s, CF_3) ppm. MS (EI) *m/z* 212.93 $[M\text{-}H_2O]^+$.

*3.8. 4,4,4-Trifluoro-1-(furan-2-yl)-3,3-dihydroxy-2-(hydroxyimino) butan-1-one (**3g**)*

^{1}H NMR (500 MHz, DMSO-d_6): δ = 6.75 (m, 1H, Ar), 7.34 (m, 1H, Ar), 7.84 (s, 2H, 2 OH), 8.04 (m, 1H, Ar), 11.95 (s, 1H, NOH) ppm. ^{19}F NMR (470 MHz, DMSO-d_6): δ = −82.0 (s, CF_3) ppm.

*3.9. 4,4,4-Trifluoro-1-(furan-2-yl)-2-(hydroxyimino)butan-1,3-dione (**2g**)*

^{1}H NMR (500 MHz, DMSO-d_6): δ = 6.83 (m, 1H, Ar), 7.58 (m, 1H, Ar), 8.17 (m, 1H, Ar), 14.52 (s, 1H, NOH) ppm. ^{19}F NMR (470 MHz, DMSO-d_6): δ = −71.6 (s, CF_3) ppm.

*3.10. 4,4,4-Trifluoro-3,3-dihydroxy-2-(hydroxyimino)-1-(pyridin-4-yl)butan-1-one (**3h**)*

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.75 (m, 2H, Ar), 8.07 (s, 2H, 2 OH), 8.86 (m, 2H, Ar), 12.13 (s, 1H, NOH) ppm. ^{19}F NMR (470 MHz, DMSO-d_6): δ = −82.1 (s, CF_3) ppm.

*3.11. 4,4,4-Trifluoro-2-(hydroxyimino)-1-(pyridin-4-yl)butan-1,3-dione (**2h**)*

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.78 (m, 2H, Ar), 8.92 (m, 2H, Ar), 14.66 (s, 1H, NOH) ppm. ^{19}F NMR (470 MHz, DMSO-d_6): δ = −71.6 (s, CF_3) ppm.

*3.12. Acyl nitriles **4** (general procedure)*

Compound **3** (20 mmol) and Ac_2O (20 mmol) in 20 ml of $CHCl_3$ was refluxed for 1 h. Then 25 mL of water was added to quench the reaction. Organic layer was washed with brine and dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure the residue was purified by column chromatography on silica gel (eluent $CHCl_3$/hexane = 3:1). Spectral data (^{1}H NMR spectra) and physico-chemical properties (mp or bp) were in accordance with the literature [7].

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