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Article

A Solvent-free Synthesis of β-Enamino Trihalomethyl Ketones

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Este trabalho apresenta uma metodologia, ambientalmente adequada e mais econômica em relação àquelas descritas na literatura, para a obtenção de uma série de vinte e seis 4-amino-1,1,1-trialo-3-alquen-2-onas [$CX_3C(O)CH=C(R^1)NR^2R^3$, com X = F, Cl, R^1 = H, Me, e R^2/R^3 = H/Ph, H/4-F-Ph, H/Bn, H/$(CH_2)_2$OH, Me/Ph, Me/Bu, Et/Et, -$(CH_2)_4$-], a partir da reação de 1,1,1-trialo-4-alcóxi-3-alquen-2-onas com aminas primárias e secundárias, na ausência de solvente, a temperatura ambiente e em cinco minutos (rendimentos de 73-99%).

An efficient *green* procedure to prepare a series of twenty-six 4-amino-1,1,1-trihalo-3-alken-2-ones [$CX_3C(O)CH=C(R^1)NR^2R^3$, where X = F, Cl, R^1 = H, Me, and R^2/R^3 = H/Ph, H/4-F-Ph, H/Bn, H/$(CH_2)_2$OH, Me/Ph, Me/Bu, Et/Et, -$(CH_2)_4$-] from the solvent-free reaction of 1,1,1-trihalo-4-alkoxy-3-alken-2-ones with primary and secondary amines at room temperature for five minutes is reported (yields of 73-99%).

Keywords: solvent-free, enaminones, enones, trihalomethyl-compounds, green chemistry

Introduction

β-Enaminones and β-enamino esters are useful synthetic buildings blocks for various pharmaceuticals[1,2] and bioactive heterocycles.[3] They have been used for the preparation of different important antibacterial,[4] anticonvulsant,[5] anti-inflammatory[5] and antitumour agents.[6] They are also the intermediates for the synthesis of several aminoacids,[7-9] aminols,[8] peptides and alkaloids.[10] It is well-known that the introduction of trihalomethyl groups into heterocyclic compounds may have a significant influence on their biological and physical properties. The most convenient method to construct trihalomethylated compounds is to use halogen-containing building blocks as starting reagents.[11,12] Therefore, the development of synthetic methods for trihalogenated synthetic building blocks has been an important field in organic synthesis. β-enamino trihalomethyl ketones are commonly prepared from β-alkoxy vinyl trihalomethyl ketones[12] or acetylenes.[13] One of the most effective methods used to synthesize β-enamino trihalomethyl ketones is the amination reaction of β-alkoxyvinyl trifluoro[chloro]methyl ketones.[14] Vdovenko *et al.*[15] have obtained four trihalomethylated enaminones and one non-halogenated enaminone by a similar route. Recently, we reported the synthesis of trihalomethyl substituted enaminones and trihalomethylated isoxazolines obtained from by the ultrasound promoted reaction of 1,1,1-trihalo-4-alkoxy-3-alken-2-ones with aniline in aqueous media.[16] We also published the preparation of trihalomethyl substituted β-ethoxy-β-enamino ketones from the reaction of 1,1,1-trihalo-4,4-dietoxy-3-alken-2-ones with amines in solvent-free conditions and the utility of this intermediates to obtainment of N-azolyl amines.[17] Another general method for the synthesis of trihalomethylated enaminones is from trifluoromethylated enones using trifluoropropynyl lithium with N-methoxy-N-methylbenzamide (Weinreb benzamide).[18] Unfortunately, in general, the processes to synthesize trihalomethyl substituted β-enamino ketones suffers from limitations, such as long reaction times, multi-step reactions and tedious work-up.[19,20] Thus, because of the applicability of β-enamino trihalomethyl ketones as a promising building blocks for the synthesis heterocycles,[21,22] a simple, general and high yielding one-pot approach for the synthesis of this enaminones is highly desirable. In particular, it has been shown that syntheses which are carried out in solvent-free conditions are often rapid, regio- or chemoselective, occur in high yields and have environmental and economic advantages.

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Considering our interest to explore new and green routes in organic synthesis, we decided to investigate the synthesis of β-enamino trihalomethyl ketones by the solvent-free reaction of 1,1,1-trihalo-4-alkoxy-3-alken-2-ones with primary and secondary amines.

Results and Discussion

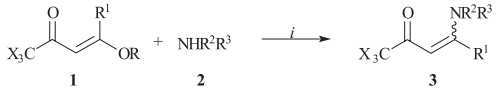
The starting material, 1,1,1-trihalo-4-alkoxy-3-alken-2-ones, **1**, was synthesized from the reaction of the respective enol ether and trifluoroacetic anhydride or trichloroacetyl chloride.[12] The amines were purchased commercially.

To establish the potential of the synthesis of β-enamino trihalomethyl ketones in solvent-free conditions, we began our investigation by reaction of 1,1,1-trifluoro-4-alcoxy-3-buten-2-one **1a** with aniline without solvent. In order to evaluate if this conditions was better than others solvents, we performed the same reaction by screening a variety of different solvents. The effect of the solvent on the reaction of enones **1** and amines **2** under some solvents was summarized in Table 1**.**

Table 1. Reactions conditions used for synthesis of β-enamino trihalomethyl ketones

Entry	Solvent	T / °C	time / min	Yield / %
1	Solvent-free	0	5	92
2	Ethanol	25	5	20
3	Ethanol	0	5	49
4	Ethanol	0	10	66
5	Acetonitrile	0	15	40

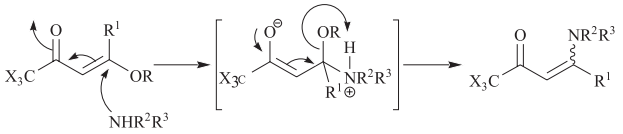
Taking into account that this reaction is considered a nucleophilic addition/substitution, we carried out the reaction in polar solvents. When ethanol was used as solvent at room temperature, the yield of enaminones obtained was 20%. However, when the reaction was performed at 0 °C in ethanol, and it was stirring for 5 min, we obtained the yield of **3a** increased to 49%. At the same temperature, but a reaction time of 10 min, the yield of **3a** was increased to 66%. When the reaction was carried out in acetonitrile at 0 °C and, after stirring for 15 min, the yield of **3a** remained similar that obtained in ethanol. Finally, when the reaction was carried out under solvent-free conditions, a significant improve on the yield was observed (yield > 90%, Table 1). Several enone:amine molar ratios were tested, and the best ratio we found was 1:1. Thus, the typical experiment was established by the addition of the appropriate amine **2** to 1,1,1-trihalo-4-alkoxy-3-alken-2-one **1** at 0 °C, and the mixture was stirred at room temperature for 5 minutes (Scheme 1). After the reaction time, the desired products were obtained in the pure form and side products were not observed. The results summarized in Table 2 show that primary and secondary amines, both aromatic and aliphatic, with linear and branched *N*-substituents reacted without any significant difference to give the corresponding β-enamino trifluoro[chloro]methyl ketones in good yields. In the preparation of some compounds (**3a**, **3o** and **3v**), where the less reactive amine was used, the reaction was performed in water as solvent and under ultrasound irradiation for 15-20 min (entries 1, 15, and 22, Table 2). The isolated products were characterized by their melting points, ^{1}H and ^{13}C NMR, GC/MS spectral analysis.



i: 0 - 25 °C, 5 min, solvent-free (see Table 2)

Scheme 1.

In comparison with a procedure used by Hojo and coworkers,[12,14] the method shown here by us presented the advantages of decrease of reaction time, absence of solvent and easy work-up. As regards to previous works published by us, for example, using ultrasound irradiation, this procedure is even faster and to execute this procedure do not it necessary the ultrasound equipment, and the synthesis can be proceed in large scale. Recently, some solvent-free condensation reaction has been described in the literature,[23] and the results provide that this process is suitable due their simplicity, excellent yields and easy purification of products. In many of these studies, enaminones are the intermediate formed. Thus, based in previous works,[15] the following sequence of steps appears to afford a satisfactory explanation for the mode of formation of the products (Scheme 2). This reaction involves the initial attack of the amine nitrogen atom on the enone β-carbon with a charge delocalization to the carbonyl group and a subsequent elimination of the alcohol molecule.



Scheme 2.

In each case, the stereochemistry of the 4-amino-1,1,1-trihalo-3-alken-2-ones **3** was assigned based on the ^{1}H NMR spectroscopy. The downfield peak of the amino protons (10-12 ppm) in compounds **3a-d** and **3o-r** suggests

Table 2. Synthesis of β-enamino trihalomethyl ketones **3** from the reaction of 1,1,1-trihalo-4-alkoxy-3-alken-2-ones **1** with primary and secondary amines **2**

Entry	X	R	R^1	R^2	R^3	Product	Yield / (%)[a]	Lit. yield / (%)[a]
1[b]	F	Me	Me	H	Ph	**3a**	93	80[15]
2	F	Me	Me	H	4-F-C_6H_4	**3b**	91	–
3	F	Me	Me	H	Bn	**3c**	92	–[25]
4	F	Me	Me	H	$(CH_2)_2OH$	**3d**	89	–[26]
5	F	Me	Me	Me	Ph	**3e**	93	–
6	F	Me	Me	Me	Bu	**3f**	76	–
7	F	Me	Me		-$(CH_2)_4$-	**3g**	97	–
8[b]	F	Et	H	H	Ph	**3h**	92	94,[15] 90,[27] 88[12]
9	F	Et	H	H	4-F-C_6H_4	**3i**	90	84[27]
10	F	Et	H	H	Bn	**3j**	87	–[28]
11	F	Et	H	Me	Ph	**3k**	88	95[29]
12	F	Et	H	Me	Bu	**3l**	89	–
13	F	Et	H	Et	Et	**3m**	79	96,[30] 95[29]
14	F	Et	H		-$(CH_2)_4$-	**3n**	89	–[25]
15[b]	Cl	Me	Me	H	Ph	**3o**	93	90,[15] 95[12]
16	Cl	Me	Me	H	4-F-C_6H_4	**3p**	87	–
17	Cl	Me	Me	H	Bn	**3q**	81	–[31]
18	Cl	Me	Me	H	$(CH_2)_2OH$	**3r**	89	–
19	Cl	Me	Me	Me	Ph	**3s**	88	–[32]
20	Cl	Me	Me	Me	Bu	**3t**	73	–
21	Cl	Me	Me		-$(CH_2)_4$-	**3u**	89	–
22[b]	Cl	Et	H	H	Ph	**3v**	99	88[15]
23	Cl	Et	H	H	4-F-C_6H_4	**3w**	91	–
24	Cl	Et	H	H	Bn	**3x**	87	–
25	Cl	Et	H	Me	Bu	**3y**	83	–
26	Cl	Et	H	Et	Et	**3z**	79	–

[a]Yield of isolated compound. [b]Reaction performed in water as solvent and under ultrasound irradiation for 15-20 minutes.

the existence of an intramolecular hydrogen bond and, therefore, a *cis*-relationship between the NH and C=O groups, for which reason a *Z*-configuration was deduced. The formation of the *Z*-isomer in compounds **3h-j** and **3v-x** was proven by the coupling constants of the hydrogen atoms attached on the double bond (J_{H3-H4} = 7.1-7.9 Hz) and also by a distinct splitting of the H4 atom on the amino group NH (12.9-13.5 Hz) fixed *via* an intramolecular hydrogen bond.[7] The *E*-configuration of the β-enamino trihalomethyl ketones **3k-n** and **3y-3z** was confirmed by the J_{H3-H4} coupling constants (12.4-12.8 Hz) of these compounds. The *Z*- and *E*-configurations proposed were confirmed by X-ray diffraction for compound **3q** and **3u** (Figure 1).[24]

Conclusions

We reported the reactions of 1,1,1-trihalo-4-alkoxy-3-alken-2-ones with primary and secondary amines under solvent-free conditions. A range of 4-amino-1,1,1-trihalo-4-alkoxy-3-alken-2-ones were obtained in good to excellent yields. The reactions of 1,1,1-trihalo-4-alkoxy-3-alken-2-ones with amines were also studied and the stereochemistry of the products were dependent on the amines used. Moreover, to shorten the reaction time in relation to conventional methods, this procedure does not use organic solvents, which minimizes environmental impact and costs, and increases operational safety.

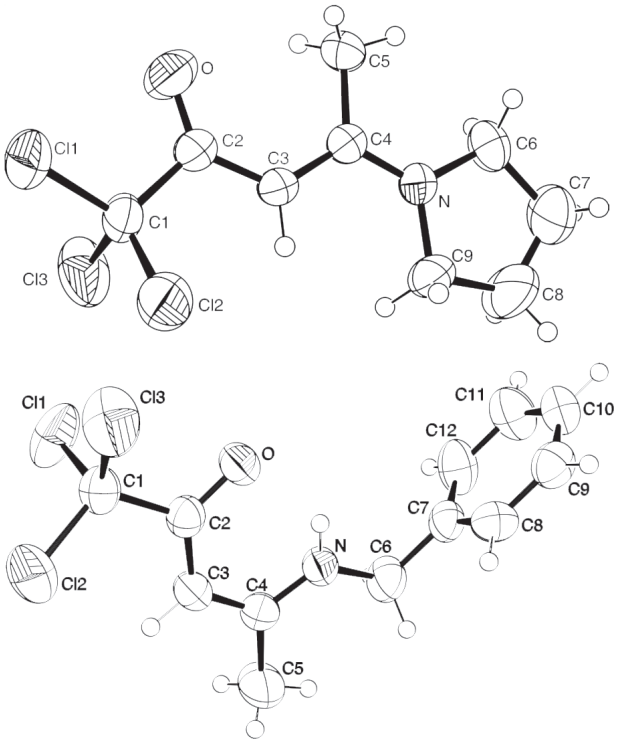


Figure 1. ORTEP of enaminones **3u** and **3q**.

Experimental

General

Unless otherwise indicated, all common reagents and solvents were used as obtained from commercial suppliers without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 400 spectrometer (^{1}H at 400.13 MHz and ^{13}C at 100.62 MHz) at 298 K with a digital resolution of ± 0.01 ppm, with 0.5 mol L^{-1} solutions in $CDCl_3$ as solvent, containing TMS as internal standard. All spectra were acquired in a 5 mm tube, at natural abundance. *J* values are given in Hz. Mass spectra were registered in a HP 5973 MSD connected to a HP 6890 GC and interfaced by a Pentium PC. The CG was equipped with a split-splitless, injector, auto sampler, cross-linked HP-5 capillary column (30 m, 0.32 mm of internal diameter), and helium was used as the carrier gas.

*General procedure for the synthesis of the 4-amino-1,1,1-trihalo-3-alken-2-ones (**3a-z**)*

The appropriate amine **2** (2 mmol) was added to enone **1** (2 mmol) at 0 °C. The mixture equivalent was stirred at room temperature for 5 minutes. The product obtained, after undergoing reduced pressure for 1 hour, was pure enough for most purposes as indicated by physical and spectroscopic data. The solid products were recrystallized from hexane as solvent. Physical and spectroscopic data for compounds **3**, see literature cited in the Table 2. The compounds **3b**,**e**,**f**,**g**,**l**,**p**,**r**,**t**,**u**,**w**,**x**,**y**,**z** are not reported in the literature and physical and spectroscopic data are described below.

*(Z)-1,1,1-Trifluoro-4-(4-fluorophenylamino)pent-3-en-2-one (**3b**)*

mw 247.19; mp 68-70 °C (from hexane); δ_H (400 MHz; $CDCl_3$; Me_4Si) 2.11 (3 H, s, Me), 5.54 (1H, s, CH), 7.15-7.43 (4 H, m, Ph) and 11.45 (1H, s, NH); δ_C (J_{CF}, Hz) (100 MHz; $CDCl_3$; Me_4Si) 20.1(CH_3), 90.9 (CH), 116.3, 116.6 (q, $^{1}J_{CF}$ 288), 127.3 (CH), 133.0(CH), 161.6 (d, $^{1}J_{CF}$ 248), 168.2 (C) and 176.8 (q, $^{2}J_{CF}$ 33); *m/z* (EI) 247 (M^+, 49%), 178 (100), 95 (34) and 75 (24). Anal. Calc. for $C_{11}H_9NOF_4$: C, 53.45; H, 3.67; N, 5.67. Found: C, 53.20; H, 3.65; N, 5.64.

*(E)-1,1,1-Trifluoro-4-(methylphenylamino)pent-3-en-2-one (**3e**)*

mw 243.23; Oil; δ_H (400 MHz; $CDCl_3$; Me_4Si) 2.39 (3H, s, Me), 3.35 (3H, s, NMe), 5.41 (1H, s, CH) and 6.63-7.46 (5H, m, Ph); δ_C (J_{CF}, Hz) (100 MHz; $CDCl_3$; Me_4Si) 19.1(CH_3), 41.6 (CH_3), 89.6 (CH), 117.8 (q, $^{1}J_{CF}$ 293), 126.4 (CH), 128.4 (CH), 129.1 (CH), 129.9 (CH), 168.0 (C) and 176.0 (q, $^{2}J_{CF}$ 31); *m/z* (EI) 243 (M^+, 45%), 147 (100), 146 (48), 131 (64), 77 (82) and 56 (97). Anal. Calc. for $C_{12}H_{12}NOF_3$: C, 59.26; H, 4.97; N, 5.76. Found: C, 58.81; H, 4.94; N, 5.72.

*(E)-4-(Butylmethylamino)1,1,1-trifluoropent-3-en-2-one (**3f**)*

mw 223.24; Oil; δ_H (400 MHz; $CDCl_3$; Me_4Si) 0.96 (3H, t, Me), 1.36 (2H, m, CH_2), 1.57 (2H, m, CH_2), 2.60 (3H, s, Me), 3.04 (3H, s, NMe), 3.42 (2H, t, NCH_2) and 5.19 (1H, s, CH); δ_C (J_{CF}, Hz) (100 MHz; $CDCl_3$; Me_4Si) 13.4 (CH_3), 16.4 (CH_3), 19.6 (CH_3), 30.1(CH_2), 38.8 (CH_2), 52.0 (CH_2), 86.6 (CH), 117.9 (q, $^{1}J_{CF}$ 293), 167.5 (C) and 174.7 (q, $^{2}J_{CF}$ 31); *m/z* (EI) 223 (M^+, 33%), 180 (46), 154 (85), 112 (74) and 56 (100). Anal. Calc. for $C_{10}H_{16}NOF_3$: C, 53.80; H, 7.22; N, 6.27. Found: C, 53.42; H, 7.19; N, 6.23.

*(E)-1,1,1-Trifluoro-4-(pyrrolidin-1-yl)pent-3-en-2-one (**3g**)*

mw 207.19; mp 69-71 °C (from hexane); δ_H (400 MHz; $CDCl_3$; Me_4Si) 2.00 (4H, m, 2 × CH_2), 2.60 (3H, s, Me), 3.40 (2H, t, NCH_2), 3.50 (2H, t, NCH_2) and 5.10 (1H, s, CH); δ_C (J_{CF}, Hz) (100 MHz; $CDCl_3$; Me_4Si) 18.5 (CH_3), 24.6 (CH_2) , 24.9(CH_2), 48.8(CH_2), 49.1(CH_2), 87.3(CH), 118.1 (q, $^{1}J_{CF}$ 292), 166.0(C) and 174.7 (q, $^{2}J_{CF}$ 30); *m/z* (EI) 207 (M^+, 35%), 138 (100), 110 (17) and 70 (30). Anal. Calc. for $C_9H_{12}NOF_3$: C, 52.17; H, 5.84; N, 6.76. Found: C, 51.85; H, 5.80; N, 6.72.

*(E)-4-(Butylmethylamino)-1,1,1-trifluorobut-3-en-2-one (**3l**)*

mw 209.21; Oil; δ_H (400 MHz; $CDCl_3$; Me_4Si) 0.95 (3H, t, Me), 1.33 (2H, m, CH_2), 1.61 (2H, m, CH_2), 2.94 (3H, s, NMe), 3.37 (2H, t, NCH_2), 5.59 (1H, d, CH) and 7.83 (1H, d, J 6.8); δ_C (J_{CF}, Hz) (100 MHz; $CDCl_3$; Me_4Si) 13.4 (CH_3), 19.4 (CH_3), 30.3 (CH_2), 35.6 (CH_2), 50.4 (CH_2), 86.9 (CH), 117.7 (q, $^{1}J_{CF}$ 291), 156.3 (CH) and 176.9 (q, $^{2}J_{CF}$ 33); *m/z* (EI) 209 (M^+, 40%), 166 (73), 140 (100) and 98 (70). Anal. Calc. for $C_9H_{14}NOF_3$: C, 51.67; H, 6.75; N, 6.70. Found: C, 51.34; H, 6.70; N, 6.65.

*(Z)-1,1,1-Trichloro-4-(4-fluorophenylamino)pent-3-en-2-one (**3p**)*

mw 296.55; mp 68-70 °C (from hexane); δ_H (400 MHz; $CDCl_3$; Me_4Si) 2.10 (3H, s, Me), 5.89 (1H, s, CH), 7.08-7.18 (4H, m, Ph) and 11.05 (1H, s, NH); δ_C (J_{CF}, Hz) (100 MHz; $CDCl_3$; Me_4Si) 20.5 (CH_3), 88.4 (CH), 96.9 (CCl_3),

116.3 (CH), 116.5 (CH), 127.2 (CH), 133.4 (CH), 161.4 (d, $^1J_{CF}$ 248), 167.2 (C), 181.2 (C=O); *m/z* (EI) 295 (M^+, 4%), 232 (18), 178 (100) and 95 (28). Anal. Calc. for $C_{11}H_9NOFCl_3$: C, 44.55; H, 3.06; N, 4.72. Found: C, 44.18; H, 3.03; N, 4.68.

(Z)-1,1,1-Trichloro-4-(2-hydroxyethylamino)pent-3-en-2-one ***(3r)***

mw 246.51; mp 80-82 °C (from hexane); δ_H (400 MHz; $CDCl_3$; Me_4Si) 2.14 (3H, s, Me), 3.53 (2H, q, NCH_2), 3.84 (2H, t, J 5.2, OCH_2), 5.71 (1H, s, CH) and 10.85 (1 H, s, NH); δ_C (100 MHz; $CDCl_3$; Me_4Si) 19.9(CH_2) , 45.8(CH_2), 60.6(CH_2), 86.8 (CH) , 97.1 (CCl3), 169.7 (C) and 179.9; *m/z* (EI) 245 (M^+, 3%), 182 (26), 128 (100), 82 (31) and 54 (16). Anal. Calc. for $C_7H_{10}NO_2Cl_3$: C, 34.11; H, 4.09; N, 5.68. Found: C, 33.76; H, 4.05; N, 5.60.

(E)-4-(Butylmethylamino)-1,1,1-trichloropent-3-en-2-one ***(3t)***

mw 272.60; Oil; δ_H (400 MHz; $CDCl_3$; Me_4Si) 0.97 (3H, t, Me), 1.37 (2H, m, CH_2), 1.61 (2H, m, CH_2), 2.58 (3H, s, Me), 3.07 (3H, s, NMe), 3.39 (2 H, t, NCH_2) and 5.65 (1H, s, CH); δ_C (100 MHz; $CDCl_3$; Me_4Si) 13.7 (CH_3), 19.9 (CH_3), 27.8 (CH_3), 32.8 (CH_2), 38.9 (CH_2), 49.2 (CH_2), 84.7(CH), 99.8 (CCl_3), 167.5 (C) and 178.8 (C=O); *m/z* 271 (EI) (M^+, 26%), 236 (26), 208 (100), 154 (99) and 56 (96). Anal. Calc. for $C_{10}H_{16}NOCl_3$: C, 44.06; H, 5.92; N, 5.14. Found: C, 43.74; H, 5.87; N, 5.09.

(E)-1,1,1-Trichloro-4-(pyrrolidin-1-yl)pent-3-en-2-one ***(3u)***

mw 256.56; mp 88-90 °C (from hexane); δ_H (400 MHz; $CDCl_3$; Me_4Si) 2.03 (4H, m, 2 × CH_2), 2.58 (3H, s, Me), 3.41 (2H, t, NCH_2), 3.56 (2H, t, NCH_2) and 5.57 (1H, s, CH); δ_C (100 MHz; $CDCl_3$; Me_4Si) 18.2 (CH_2), 24.7 (CH_2), 25.1 (CH_2), 48.9 (CH_2), 49.0 (CH_2), 85.1 (CH), 99.7 (CCl_3), 165.8 (C) and 178.6; *m/z* (EI) 255 (M^+, 2%), 192 (15), 138 (100) and 55 (16). Anal. Calc. for $C_9H_{12}NOCl_3$: C, 42.14; H, 4.71; N, 5.46. Found: C, 41.74; H, 4.67; N, 5.41.

(Z)-1,1,1-Trichloro-4-(4-fluorophenylamino)but-3-en-2-one ***(3w)***

mw 282.53; mp 70-71 °C (from hexane); δ_H (400 MHz; $CDCl_3$; Me_4Si) 5.96 (1H, d, CH), 7.07-7.09 (4H, m, Ph), 7.57 (1H, dd, *J* 7.8 and 13.0 Hz, CH) and 11.32 (1 H, s, NH); δ_C (J_{CF}, Hz) (100 MHz; $CDCl_3$; Me_4Si) 88.2 (CH), 96.3 (CCl_3), 116.6 (CH), 116.9 (CH), 118.7 (CH), 135.4 (CH), 149.4 (CH), 160.1 (d, $^1J_{CF}$ 245) and 182.9 (C=O); *m/z* (EI) 281 (M^+, 12%), 218 (24), 164 (100) and 95 (32). Anal. Calc. for $C_{10}H_7NOFCl_3$: C, 42.51; H, 2.50; N, 4.96. Found: C, 42.13; H, 2.47; N, 4.91.

(Z)-4-Benzylamino-1,1,1-trichlorobut-3-en-2-one ***(3x)***

mw 278.56; Oil; δ_H (400 MHz; $CDCl_3$; Me_4Si) 4.49 (2 H, d, CH_2), 5.72 (1 H, d, CH), 7.18 (1 H, dd, *J* 7.5 and 13.5 Hz, CH), 7.20-7.40 (5 H, m, Ph) and 9.93 (1H, s, NH); δ_C (100 MHz; $CDCl_3$; Me_4Si) 85.2 (CH_2), 96.7 (CCl_3), 127.3 (CH), 128.2 (CH), 128.9 (CH), 136.2 (CH), 157.2 (CH) and 182.2 (C=O); *m/z* (EI) 277 (M^+, 10%), 214 (19), 160 (100) and 77 (53). Anal. Calc. for $C_{11}H_{10}NOCl_3$: C, 47.43; H, 3.62; N, 5.03. Found: C, 47.06; H, 3.59; N, 4.92.

(E)-4-(butylmethylamino)-1,1,1-trichlorobut-3-en-2-one ***(3y)***

mw 258.57; mp 82-84 °C (from hexane); δ_H (400 MHz; $CDCl_3$; Me_4Si) 0.96 (3H, t, Me), 1.36 (2H, m, CH_2), 1.62 (2H, m, CH_2), 2.95 (3H, s, NMe), 3.36 (2H, t, NCH_2), 5.59 (1H, d, CH) and 7.83 (1H, d, CH); δ_C (100 MHz; $CDCl_3$; Me_4Si) 13.5 (CH_3), 19.5 (CH_3), 30.5 (CH_2), 35.7 (CH_2), 58.5 (CH_2), 84.8 (CH), 98.1(CCl_3), 156.9 (CH) and 180.7 (C=O); *m/z* (EI) 257 (M^+, 4%), 194 (15), 140 (100) and 84 (22). Anal. Calc. for $C_9H_{14}NOCl_3$: C, 41.81; H, 5.46; N, 5.42. Found: C, 41.46; H, 5.37; N, 5.35.

(E)-1,1,1-Trichloro-4-diethylaminobut-3-en-2-one ***(3z)***

mw 244.55; mp 78-80 °C (from hexane); δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.24 (3 H, t, Me), 1.28 (3H, t, Me), 3.34 (2H, q, CH2), 3.40 (2H, q, CH2), 5.65 (1H, d, *J* 12.4 Hz, CH) and 7.80 (1H, d, *J* 12.4 Hz, CH); δ_C (100 MHz; $CDCl_3$; Me_4Si) 11.5(CH_3), 14.6 (CH_3), 43.2 (CH_2), 51.0 (CH_2), 84.7(CH), 98.2 (CCl_3) and 155.5 (CH); *m/z* 243 (EI) (M^+, 4%), 178 (12), 124 (100) and 82 (13). Anal. Calc. for $C_8H_{12}NOCl_3$: C, 39.29; H, 4.95; N, 5.73. Found: C, 39.00; H, 4.88; N, 5.65.

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