Halogenation of β-Alkoxyvinyl Polyhaloalkyl Ketones: A Convenient Route for the Synthesis of α-Chloro- or α-Bromo-β-alkoxyvinyl Polyhaloalkyl Ketones

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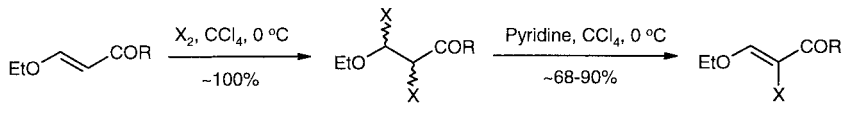
Abstract: A number of α-chloro- and α-bromo-β-alkoxyvinyl polyhaloalkyl ketones **4** and **5** were synthesized in high yields by halogenation of β-alkoxyvinyl polyhaloalkyl ketones **1** with chlorine or bromine and further dehydrohalogenation of dihalo-intermediates **2** and **3** with pyridine. The *Z* configuration of ketones **4** and **5** was deduced from X-ray analysis and NMR spectra. Some typical nucleophilic reactions of the title compounds **4** and **5** with amines were carried out to check their reactivity.

Key words: enones, halogenation, electrophilic additions, eliminations, aminations

The introduction of fluorine atoms and fluorinated groups into organic molecules often confers significant and useful changes in their chemical and physical properties. Therefore, methods for the synthesis of fluorinated compounds have received considerable interest in recent years.[1] Although direct fluorinating or polyfluoroalkylating methods are the most attractive and powerful new tools for constructing fluorinated compounds, the fluoro-containing building blocks are often the more convenient starting reagents.[2] Thus, fluorinated carbonyl and dicarbonyl compounds are often used as starting materials to obtain the desired fluoro-containing substances. Particularly (*E*)-β-alkoxyvinyl polyfluoroalkyl ketones **1** (that may be considered as synthetic equivalent of 1,3-ketoaldehydes) are accessible polyfluoroalkylated building blocks[3] for the synthesis of various fluorine-containing heterocycles, enaminones, dyes, drugs and protective reagents for amino group protection in peptide synthesis.[4] The nucleophilic reactions of enone **1b** were studied in much more detail, but only few reports have been published on the reactions of fluorinated enones **1** with electrophiles.[5]

At the same time, the electrophilic halogenation of olefins is widely used for the synthesis of various useful and accessible vinyl halide building blocks[6] and for fluoro-containing compounds as well.[7] It is obvious that the halogenation of β-alkoxyvinyl polyhaloalkyl ketones **1** will give α-chloro-, bromo-derivatives **4**, **5** having the large prospect of an application as fluorinated building blocks. The α-halo-β-alkoxyvinyl alkyl ketones were synthesized by alkylation of 2-halo-1,3-dicarbonyl compounds with various reagents such as diazomethane,[8] dimethyl sulfate[8] or ethanol.[9] The halogenation of β-alkoxyenones has not been used for the synthesis of corresponding α-haloderivatives. Two patents are available on the halogenation[10a] of enone **1b** by various reagents and the application of α-chloro- **4b** and α-bromo-derivatives **5b** for the synthesis[10b] of 3-trifluoromethyl-4-halopyrazoles as potential insecticides. However, only limited ^{1}H NMR spectra data of dihalo-intermediates **2b**, **3b**, and no data concerning the configuration of the trisubstituted C=C bond in α-chloro-, bromo-derivatives **4b**, **5b** are given in the patents.[10a] In this article, we describe the halogenation of enones **1a**–**d** which contain various polyhaloalkyl-groups, and the examination of the reactivity of α-chloro-, bromo-derivatives **4b**, **5b** in amination reactions.

We have found that chlorine and bromine readily add to the C=C bond of enones **1a**–**d**, and the mixture of diastereomeric (m.d.) dichloro- **2a**–**d** and dibromoketones **3a**–**d** are formed in quantitative yields (Scheme 1, Table 1). Formation of the diastereomeric mixture is a result of both *syn*- and *anti*-addition of halogens to (*E*)-enones **1**, where bromine gives predominantly *anti*-adducts and chlorine gives *syn*-adducts.[11]



1a-d (m.d.) **2a-d, 3a-d** **4a-d, 5a-d**

Compd	2,4	3,5
X	Cl	Br

1-5	a	b	c	d
R	CHF_2	CF_3	CCl_3	$CH(CF_3)_2$

Scheme 1

Table 1 NMR Spectra, Physical Constants and Yield of Compounds- **2a**–**e**, **3a**–**d**, **8a**, **b**

Compd	Isolated Yield[a], %	Bp, °C/mmHg or Mp, °C (solvent)	Contents of diaste-reomers, %	^{1}H NMR[b]			
				α-H, (d)	β-H, (d)	J_{HH}, Hz	Other
2a	~100	–[c]	45	4.80	5.77	6.8	1.25 (t, 3 H, *J* = 7.1, CH_3), 3.65 and 4.00 (m, 2 H, CH_2), 5.9 (t, 1 H, *J* = 53.5, CHF_2)
			55	4.93	5.83	7.4	1.32 (t, 3 H, *J* = 7.1, CH_3), 3.70 and 4.04 (m, 2 H, CH_2), 6.06 (t, 1 H, *J* = 53.5, CHF_2)
2b	~100 (70)	34–35/19	80	4.79	5.77	7.8	1.23 (t, 3 H, *J* = 7.1, CH_3), 3.63 and 4.00 (m, 2 H, CH_2)
			20	4.93	5.86	8.3	1.33 (t, 3 H, *J* = 7.0, CH_3), 3.72 and 4.06 (m, 2 H, CH_2)
2c	~100 (87)	80–81/0.5	78	5.15	5.79	8.4	1.20 (t, 3 H, *J* = 7.1, CH_3), 3.60 and 3.99 (m, 2 H, CH_2)
			22	5.31	5.87	8.5	1.34 (t, 3 H, *J* = 7.1, CH_3) 3.74 and 4.05 (m, 2 H, CH_2)
2d	~100 (97)	23–25 (hexane)	50	4.68	5.76	6.3	1.23 (t, 3 H, *J* = 7.0, CH_3), 3.62 and 3.96 (m, 2 H, CH_2), 4.68 [sept, 1 H, *J* = 7.3, $CH(CF_3)_2$]
			50	4.76	5.86	5.8	1.29 (t, 3 H, *J* = 7.1, CH_3), 3.66 and 4.04 (m, 2 H, CH_2), 4.73 [sept, 1 H, *J* = 7.3, $CH(CF_3)_2$]
2e	~90	–[c]	50	4.44	5.70	4.9	2.39 (s, 3 H, $COCH_3$), 3.58 (s, 3 H, OCH_3)
			50	4.48	5.71	6.5	2.39 (s, 3 H, $COCH_3$), 3.60 (s, 3 H, OCH_3)
3a	~100	–[c]	23	4.96	5.97	6.7	1.27 (t, 3 H, *J* = 7.1, CH_3), 3.66 and 3.99 (m, 2 H, CH_2), 6.10 (t, 1 H, *J* = 53.3, CHF_2)
			77	5.24	6.15	9.2	1.35 (t, 3 H, *J* = 7.1, CH_3), 3.71 and 4.02 (m, 2 H, CH_2), 6.08 (t, 1 H, *J* = 53.3, CHF_2)
3b	~100 (80)	36–37/1	20	4.91	6.01	7.9	1.25 (t, 3 H, *J* = 7.0, CH_3), 3.64 and 3.98 (m, 2 H, CH_2)
			80	5.21	6.12	9.4	1.36 (t, 3 H, *J* = 7.0, CH_3), 3.66 and 4.02 (m, 2 H, CH_2)
3c	~97	–[c]	30	5.27	6.05	8.5	1.21 (t, 3 H, *J* = 7.1, CH_3), 3.60 and 3.96 (m, 2 H, CH_2)
			70	5.56	6.17	9.2	1.36 (t, 3 H, *J* = 7.1, CH_3), 3.73 and 4.02 (m, 2 H, CH_2)
3d	~100 (98)	53–54 (hexane)	25	4.81	6.04	6.6	1.25 (t, 3 H, *J* = 7.1, CH_3), 3.64 and 3.96 (m, 2 H, CH_2), 4.61 [sept, 1 H, *J* = 7.4, $CH(CF_3)_2$]
			75	5.06	6.10	8.5	1.36 (t, 3 H, *J* = 7.0, CH_3, 3.69 and 4.01 (m, 2 H, CH_2), 4.51 [sept, 1 H, *J* = 7.4, $CH(CF_3)_2$]
8a	~90	–[c]	87	5.09s	–	–	2.00 (s, 3 H, CH_3), 3.54 (s, OCH_3)
			13	5.15s	–	–	2.06 (s, 3 H, CH_3), 3.61 (s, OCH_3)
8b	~90	–[c]	80	5.45	–	–	2.11 (s, 3 H, CH_3), 3.54 (s, OCH_3)
			20	5.50	–	–	2.14 (s, 3 H, CH_3), 3.55 (s, OCH_3)

[a] All compounds gave satisfactory elemental analysis data: C ± 0.26; H ± 0.19; F ± 0.23.
[b] Chemical shifts δ, ppm, coupling constants *J*, Hz.
[c] 92–98% purity (^{1}H NMR) after evaporation of the solvents in vacuum.

Ketones **2** and **3** were obtained in near quantitative yields with 92−98% purity (^{1}H NMR) after evaporation of the solvents in vacuum. In spite of the patent data[10a] concerning the instability of dihaloketones **2b** and **3b**, we have distilled ketones **2b**, **c**, **3b**, and ketones **2d**, **3d** were crystallized. The vacuum distillation of ketone **3b** is accompanied by thermal dehydrobromination (at temperatures >50 °C); 17% of α-bromoenone **5b** being formed. A more effective dehydrohalogenation of dihaloketones **2**, **3** can be carried out in the presence of base. Thus, treatment of dihaloketones **2**, **3** with pyridine yielded the corresponding α-chloro- **4a**−**d** and α-bromoenones **5a**−**d** (Scheme 1, Table 2). α-Haloenones **4**, **5** can also be obtained in "one pot", without isolation of dihaloketones **2**, **3**. Despite the formation of a diastereomeric mixture of intermediate dihaloketones **2**, **3**, the final α-haloenones **4**, **5** are obtained as single isomers. The chemical shift of the β-proton of α-haloenones **4a**−**d** and **5a**−**d** are observed in a narrow range (about 8 ppm, Table 2), which gives evidence of configurational homogeneity of these α-haloenones at C=C bond. The *Z* configuration of ketone **5d** was determined by X-ray analysis (Figure). The fragment of a molecule of ketone **5d** (from C4 to C7) has a planar structure, where bromine and oxygen (O1) atoms are in the same plane. The carbonyl group and C=C bond exist in an s-*E* conformation. IR spectra of α-haloenones **4a**−**d**, **5a**−**d** (Table 2) contain one broadened $\nu_{C=O}$ band at 1710−1693 cm^{-1} (two bands $\nu_{C=O}$ in this region are observed only in the case of difluoroacetyl-containing haloenones **4a**, **5a**), and two bands at 1621−1615 cm^{-1} and 1596−1590 cm^{-1} ascribed to $\nu_{C=C}$. The presence of two $\nu_{C=C}$ absorption bands can be explained by an equilibrium between s-*E*- and s-*Z*-conformers of *Z*-α-haloenones **4**, **5**. A more detailed examination of conformational behavior of halogenated enones is now underway.

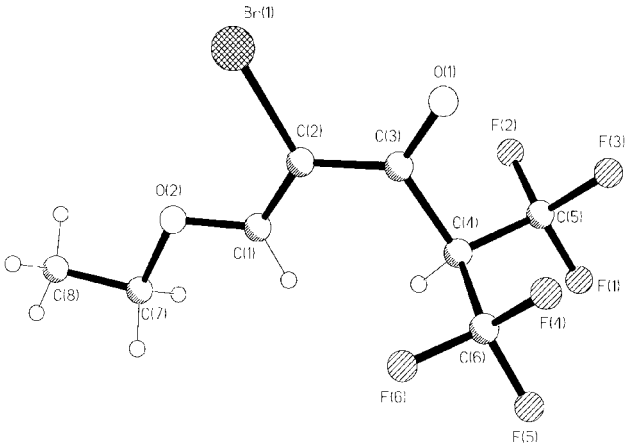
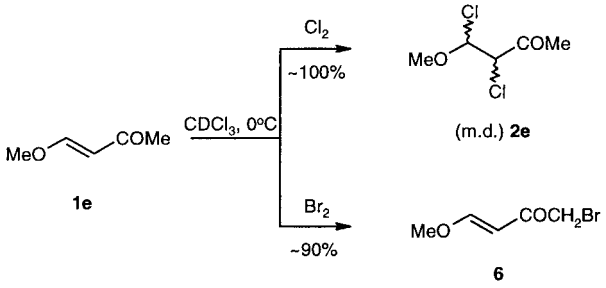


Figure Molecular structure of α-bromoenone **5d**

Selected bond lengths (Å) and torsion angles (°): Br(1)-C(2) 1.866(6), O(2)-C(1) 1.304(9), C(1)-C(2) 1.337(9), C(2)-C(3) 1.432(11), O(1)-C(3) 1.229(8), C(7)-O(2)-C(1)-C(2) 179.1(8), O(2)-C(1)-C(2)-C(3) 179.0(7), C(1)-C(2)-C(3)-O(1) −178.4(7).

A comparison of halogenation of fluorinated enone **1b** and the parent unfluorinated enone **1e** was carried out by ^{1}H NMR (Scheme 2). It was found that chlorination of (*E*)-4-methoxy-3-buten-2-one (**1e**) gives a mixture of diastereomers **2e** in quantitative yield as in the case of enones **1a**−**d**. Unexpectedly, the bromination of enone **1e** gives monobromoacetyl compound **6** in high yield, accompanied by only 3−4% of the dibromo-adduct. This result differs dramatically from results of the bromination of enones **1a**, **d** having an α-hydrogen atom in acyl group, which form dibromo-adducts **3a**, **d** only.



Scheme 2

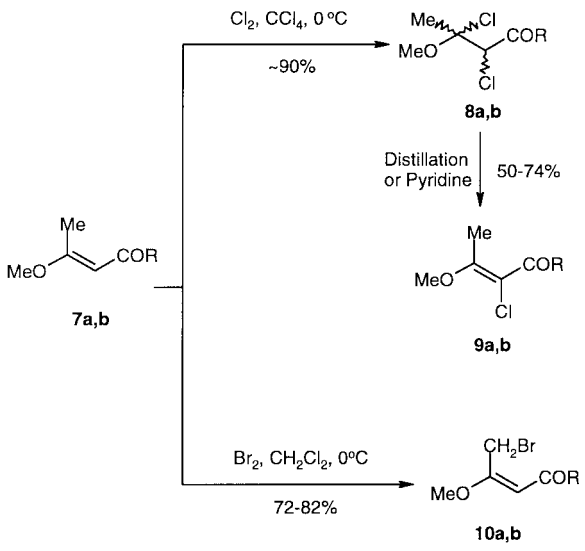
A similar difference between chlorination and bromination is observed in the halogenation of enones **7a**, **b** bearing a methyl group at the β-position of C=C bond with respect to the carbonyl group (Scheme 3). The chlorination of enones **7a**, **b** gives in high yields a mixture of diastereomers **8a**, **b**, which are dehydrochlorinated during vacuum distillation forming α-chloroenones **9a**, **b**. In this way, α-chloroenone **9b** is formed in good yield, but the yield of α-chloroenone **9a** does not exceed 20%. α-Chloroenone **9a** was obtained in good yield and of 90% purity, upon treatment of dihaloketone **8a** with pyridine. α-Chloroenones **9a**, **b** were obtained in single thermostable forms that allowed us to assign the *Z* configuration to these compounds, analogously to α-chloroenone **9** (R = Ph) in reference.[8] At the same time, bromination of enones **7a**, **b** gave at once β-monobromomethyl compounds **10a**, **b** in high yields, as a result of allylic bromination of the vinylic methyl position. However, the products **10a**, **b** contain a 5−10% admixture of β-dibromomethyl compounds,[12] inseparable by vacuum distillation.

Earlier, α-halo-β-alkoxyenones have been used as starting compounds in the heterocyclization[9,10b] or the Favorskii-rearrangement.[8] We have chosen the amination to compare the reactivity of α-chloro- **4b** and α-bromo-containing enone **5b** with their parent enone **1b**. Previously, we have shown that enones **1** reacted readily with ammonia, and primary and secondary amines yielding the corresponding β-aminovinyl polyhaloalkyl ketones.[3,4a] In order to compare the reactivity of enone **1b** with α-halo-containing enones **4b** and **5b** we studied reactions of these enones with methylamine and dimethylamine (Scheme 4, Table 2).

Table 2 Physical Constants, Yield, NMR and IR Spectra of Enones **4a**–**d**, **5a**–**d**, **6**, **9a**, **b**, **10a**, **b** and Enaminones **11b**, **c**, **e**, **f**

Compd	Bp,°C/mmHg or Mp, °C (solvent)	Yield[a],%	NMR[b]			IR, cm^{-1} (CCl_4)	
			^1H		^{19}F		
			β-H	Other		C=O	C=C
4a	49–50 (hexane)	65	7.92 (s)	1.45 (t, 3 H, *J* = 7.1, CH_3), 4.34 (q, 2 H, *J* = 7.1, CH_2), 6.10 (t, 1 H, *J* = 53.6, CHF_2)	−120.30 (d, 53.6)	1711 w 1690 m	1624 s 1604 m
4b	83–84/10[c]	80	7.90 (br q, 0.8)	1.47 (t, 3 H, *J* = 7.2, CH_3), 4.43 (q, 2 H, *J* = 7.2, CH_2)	−70.12 (d, 0.8)	1710 m	1619 s 1596 m
4c	127–128/0.5	70	8.18 (s)	1.44 (t, 3 H, *J* = 7.0, CH_3), 4.33 (q, 2 H, *J* = 7.0, CH_2)	–	1701 m	1618 m 1592 s
4d	87–88 (hexane)	81	7.88 (s)	1.45 (t, 3 H, *J* = 6.9, CH_3), 4.34 (q, 2 H, *J* = 6.9, CH_2), 5.03 [sept, 1 H, *J* = 7.2, $CH(CF_3)_2$]	−63.9 (d, 7.2)	1698 m	1621 w 1596 s
5a	45–46 (hexane)	68	8.07 (s)	1.46 (t, 3 H, *J* = 7.0, CH_3), 4.37 (q, 2 H, *J* = 7.0, CH_2), 6.10 (t, 1 H, *J* = 53.8, CHF_2)	−119.19 (d, 53.8)	1704 vw 1687 m	1617 s 1595 w
5b	103–105/19[d]	85	8.00 (br s)	1.49 (t, 3 H, *J* = 7.1, CH_3), 4.43 (q, 2 H, 7.1, *J* = CH_2)	−69.52 (br s)	1708 m	1615 s 1590 w
5c	114–115/0.5	90	8.36 (s)	1.45 (t, 3 H, *J* = 7.0, CH_3), 4.30 (q, 2 H, *J* = 7.0, CH_2)	–	1702 s	1618 vs 1586 s
5d	95–97 (hexane)	90	8.00 (s)	1.46 (t, 3 H, *J* = 7.1, CH_3), 4.37 (q, 2 H, 7.2, *J* = CH_2), 5.1 [sept, 1 H, *J* = 7.4, $CH(CF_3)_2$]	−63.91 (d, 7.4)	1693 m	1619 w 1592 s
6	–	(90)	5.99 (d, 8.9)	2.39 (s, CH_2Br), 3.59 (s, 3 H, OCH_3), 4.82 (d, 1 H, *J* = 8.8, CH)	–	–	–
9a	89–90/14	50	–	2.56 (s, 3 H, CH_3), 4.00 (s, 3 H, OCH_3)	−73.25 (s)	1696 m	1564 s
9b	140–141/16	74	–	2.49 (s, 3 H, CH_3), 3.98 (s, 3 H, OCH_3)	–	–	–
10a	77–78/10	72	–	3.86 (s, 3 H, OCH_3), 4.43 (s, 2 H, CH_2Br), 5.72 (s, 1 H, CH)	−79.03 (s)	1714 m	1593 vs
10b	116–119/0.5	82	–	3.86 (s, 3 H, OCH_3), 4.46 (s, 2 H, CH_2Br), 6.03 (s, 1 H, CH)	–	1712 m	1595 vs
11b	93–95 (hexane)	55	7.68 (d, 13.7)	3.22 (d, 3 H, *J* = 4.9, NCH_3), 5.93 (br s, 1 H, NH)	−68.32 (s)	1678 vw[e]	1623 vs[e]
11c	104–106 (hexane)	70	7.71 (d, 14)	3.26 (d, 3 H, *J* = 5.2, NCH_3), 5.97 (br s, 1 H, NH)	−68.14 (s)	1677 vw[e]	1621 vs[e]
11e	74–75/0.5	70	7.50 (s)	3.33 [s, 6 H, $N(CH_3)_2$]	−67.68 (s)	1684 m	1617 vs 1588 s
11f	43–45 (hexane)	43	7.70 (s)	3.37 [br s, 6 H, $N(CH_3)_2$]	−66.98 (s)	1679 w	1614 vs 1585 m

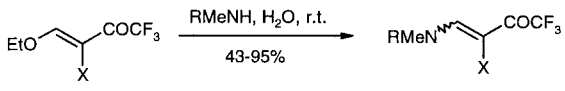
[a] All compounds gave satisfactory elemental analysis data: C ± 0.47; H ± 0.52; F ± 0.49.
[b] Chemical shifts δ, ppm., coupling constants *J*, Hz.
[c] Lit.[10a] Bp: 84–87/13 mbar.
[d] Lit.[10a] Bp: 100–102/21 mbar.
[e] In $CDCl_3$.



7-10	a	b
R	CF_3	CCl_3

Scheme 3

The reactions of enones **1b**, **4b** and **5b** with a slight excess of the amines in water proceeded with substitution of the ethoxy group by an amino group yielding enaminones **11a**–**f**. Hence, the presence of halogen atoms at α-position of enones **4b** and **5b** does not cause serious changes in the reaction route, but results in a decrease of yields from 85–95% for enaminones **11a**, **d** (X = H)[13] to 43% for enaminone **11b** and 55% for enaminone **11f**. The ^{1}H NMR spectra of enaminones **11b**, **c**, **e**, **f** (Table 2) show that they exist only as one isomer in $CDCl_3$ solution. Previously,[13,14] we have published detailed investigations on the stereochemistry of trifluoromethyl containing enaminones **11a**, **d**. A comparison of β-H and NH chemical shifts of enaminones **11a**, **b**, **c** and their behavior with increasing solvent polarity (Table 3) indicate the *Z* configuration of enaminones **11b**, **c** (*E* configuration between amino and trifluoroacetyl groups), that may be explained by steric hindrance between the α-halogen atom and the trifluoromethyl group in *E*-s-*Z*-isomer of enaminones **11b**, **c** with intramolecular hydrogen bond. Enaminones **11e**, **f** exist in the *Z* configuration, which is a common feature for *N*,*N*-dialkylenaminones. A more complete investigation of the stereochemistry of enaminones **11b**, **c**, **e**, **f** depending on the nature of the substituent at α-position is now underway.



1b,4b,5b **11a-f**

11	a	b	c	d	e	f
X	H	Cl	Br	H	Cl	Br
R	H	H	H	Me	Me	Me

Scheme 4

In summary, we have synthesized a number of useful fluoro-containing building blocks – α-chloro-, bromo-β-alkoxyvinyl polyhaloalkyl ketones, by the halogenation of accessible β-alkoxyvinyl polyhaloalkyl ketones with chlorine and bromine and further dehydrohalogenation of dihalo-intermediates. Halogenation of Me-containing enones **1e** and **7a**, **b** proceeds by two different routes: chlorination gives dichloro-adducts with the assistance of C=C bond, whereas the bromination results in bromination of the methyl group. It was shown that an amination of these available and convenient fluorinated enones **4b**, **5b** differ insignificantly from enone **1b**.

Starting materials were of the highest commercial quality and were used without further purification. ^{19}F NMR chemical shifts are reported in ppm, negative upfield relative to internal $CFCl_3$, ^{1}H NMR chemical shifts are reported in ppm, positive downfield relative to internal TMS; spectra were recorded in $CDCl_3$ at 282.24 MHz and 300 MHz (Varian VXR-300), respectively. GC analysis were obtained using SE-30 (5%) column (3.3 m × 3 mm) on Chrom-5 (Prague, Czechoslovakia) with FID and N_2 as gas-carrier. Starting enones were obtained by the reaction of the corresponding acid chlorides with alkyl vinyl ethers: enones **1a**, **d**,[3] enone **1b**, **c**,[15] enone **7a**, **b**.[16] Enone **1e** was purchased from Fluka.

4,5-Dichloro-5-ethoxy-1,1,1-trifluoro-2-trifluoromethylpentan-3-one (2d); Typical Procedure for Dihaloketones 2, 3 and 6

To the solution of enone **1d** (1.17 g, 4.7 mmol) in CCl_4 (4 mL, for **6** in $CDCl_3$) was added 0.5 M solution of chlorine in CCl_4 (10 mL, 5 mmol) at 0 °C with stirring. The reaction mixture was stirred for 1 h at 20 °C, then the solvent was evaporated. The residue was distilled in vacuum or crystallized. Yields, physical constants and NMR data are shown in Table 1.

(*Z*)-3-Bromo-4-ethoxy-1,1,1-trichlorobut-3-en-2-one (5c); Typical Procedure for α-Haloenones 4, 5, 8–10

To the solution of enone **1c** (2.61 g, 12 mmol) in CH_2Cl_2 (5 mL) was added bromine (2.1 g, 13 mmol) at 0 °C with the stirring. After 1 h, pyridine (1.04 g, 13 mmol) was added to the reaction mixture (except for **10**) at 0 °C with stirring. The reaction mixture was stirred for 1–2 h at 20 °C, H_2O (50 mL) was added, and the aqueous phase was extracted with hexane (3 × 10 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated. The residue was distilled in vacuum or crystallized. Yields, physical constants and NMR data are shown in Table 2.

3-Bromo-4-methylamino-1,1,1-trifluorobut-3-en-2-one (11c); Typical Procedure for Enaminones 11a–f

Enone **5b** (1.06 g, 4.3 mmol) was added to the solution of RNH_2 (0.19 g, 6 mmol) in H_2O (1 mL) under stirring at 0 °C. The mixture was stirred for 1–2 h at r.t., the product was filtered, and crystallized or distilled in vacuum. Yields, physical constants and NMR data are shown in Table 2.

Table 3 Selected ^{1}H NMR Spectra Data (δ, ppm) for Enaminones **11a–c** in Various Solvents

Compds	X	$CDCl_3$		CD_3CN or $(CD_3)_2CO$		$(CD_3)_2SO$	
		β-CH	NH	β-CH	NH	β-CH	NH
(*Z*)-**11a**	H	7.10	10.17	7.29[a]	10.09[a]	7.45	10.05
(*E*)-**11a**	H	7.97	5.98	7.93[a]	6.78[a]	7.90	8.64
(*Z*)[b]-**11b**	Cl	7.68	5.93	–	–	7.99	8.46
(*Z*)[b]-**11c**	Br	7.71	5.97	8.02[c]	7.50[c]	8.01	8.32

[a] In CD_3CN.
[b] *E*-Configuration between amino and trifluoroacetyl groups.
[c] In $(CD_3)_2CO$.

X-ray Crystallographic Data for Compound 5d

The crystals of α-bromoenone **5d** were obtained by crystallization from hexane.

$C_8H_7BrF_6O_2$, M = 329.05, monoclinic, a = 6.928(1), b = 15.893(3), c = 10.902(2) Å, β = 90.94(3), V = 1200.2(4) Å^3, space group $P2_1/c$, Z = 4, D_c = 1.82 g·cm^{-3}, μ = 5.37 mm^{-1}, F(000) = 640, crystal dimensions 0.28 × 0.30 × 0.40 mm. The intensities of 1636 reflections were measured on a Enraf-Nonius CAD4 diffractometer (CuK_α-adiation, T = 293 K, $4 < \theta < 60^0$, 1478 unique reflections). The structure was solved by direct methods[17] and refined on F^2 by full-matrix least-squares techniques[18] in anisotropic approximation (1308 reflection with $I > 2\sigma(I)$, 155 variables, observations/variables = 8.4, weighting scheme $w^{-1} = \sigma^2(F_o^2)+(0.0727P)^2+1.0938P$, where $P = (F_o^2+2F_c^2)/3$). All hydrogen atoms were placed geometrically and included in the final refinement with the fixed positional and thermal parameters. Convergence was obtained at R(F) = 0.056, $R_w(F^2)$ = 0.131, GOF = 1.054, Δρ(min/max) = –0.27/0.56 e·Å^{-3}. Atomic coordinates and further crystallographic details have been deposited at the Cambridge Crystallographic Data Centre, deposition number 146922, and copies of this data can be obtained in application to CCDC, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK (fax:+44 1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

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