Synthesis of perfluoroalkyl-containing tri- and tetradentate β-amino enones*

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Reactions of perfluoroalkyl-containing aliphatic 1,3-diketones with triethyl orthoformate afforded a number of β-ethoxy enones. Their reactions with *o*-phenylenediamine gave novel perfluoroalkyl-containing tridentate β-amino enones and tetradentate bis(β-amino enones) in high yields.

Key words: perfluoroalkyl-containing 1,3-diketones, β-ethoxy enones, β-amino enones, bis(β-amino enones), *o*-phenylenediamine.

Achievements of coordination chemistry are largely associated with creation of new types of ligands. Modification of known ligand systems such as 1,3-diketones and their heteroanalogs (thioxo ketones, amino enones, amino enethiones, *etc*.) also considerably contributes to the chemistry of complex compounds.[1] Introduction of fluorine atoms into 1,3-dicarbonyl compounds substantially changes the electron density distribution, which in turn greatly affects their chemical and physical properties.[2] In particular, this increases the acidities of 1,3-dicarbonyl compounds, stabilizes their complexes with transition metal ions, and increases the Lewis acidities of the complexes, which proved to be very useful for the design and production of molecular magnetics.[3]

Perfluoroalkyl-containing bis(β-amino enones) are tetradentate ligands, in which the N_2O_2 coordination sphere is analogous to that of bis(salicylaldimines), whose complexes with various metals are being extensively investigated[4] and have been found to be efficient catalysts,[5] potential materials with nonlinear optical characteristics,[6,7] models of coenzyme B_{12} [8—10], *etc*.

Bis(β-amino enones) can be relatively easily obtained from 1,3-diketones and diamines;[2,11] however, reactions of polyfluoroalkyl-containing 1,3-diketones occur smoothly only with aliphatic diamines; in the case of *o*-phenylenediamine (PDA), polyfluoroalkyl-1,5-benzodiazepines or acid decomposition products are usually obtained.[2] The reaction of PDA with 2-polyfluoroacylcycloalkanones is the exception, which yields monoamino enones under mild conditions.[12] The formation of nickel(II) complexes in reactions of fluoroalkyl-containing 2-arylazo-β-amino enones with PDA under conditions of template synthesis has been reported.[13] At the same time, introduction of an aromatic fragment lengthens the conjugation chain in the molecule, which can affect the optical properties of both the ligand itself and its complexes. The spatial structure of the ligand and, probably, the coordination of metal ions change as well.

Trifluoromethyl-containing bis(β-aminovinyl ketone) with a 1,2-phenylene fragment obtained by a reaction of PDA with β-ethoxyvinyl trifluoromethyl ketone (2 equiv.)[14] has been until recently the only example of the synthesis of such perfluoroalkyl-containing bis(β-amino enones). Tridentate mono-β-amino enones have been reported to be easily accessible by reactions of PDA with β-aryl-β-methoxyvinyl trifluoromethyl ketones.[15]

The reaction of trifluoroacetic anhydride with vinyl ethers or aliphatic dimethyl ketals in the presence of pyridine is an efficient route to trifluoromethyl β-alkoxy enones.[16,17] Later, this methodology has been extended to the synthesis of a large number of alkyl-, aryl-, and hetaryl-containing trihalomethyl β-methoxy enones.[18,19] Acylation of vinyl ethers with perfluoro carboxylic acid halides has been used to introduce longer fluoroalkyl substituents.[20] It is known that acid-catalyzed reactions of nonfluorinated 1,3-diketones with triethyl orthoformate give β-ethoxy enones.[21] However, for fluoroalkyl-containing 1,3-diketones, which are easily obtained by the Claisen condensation, this reaction with orthoformates has not been documented until recently, although the formation of 1,1-dimethoxy-2-trifluoroacetylcyclohexane in the reaction of 2-trifluoroacetylcyclohexanone with trimethyl orthoformate has been reported.[22]

In the present study, we showed that reactions of 1,3-diketones **1** with triethyl orthoformate in the presence of strong mineral acids are a suitable route to perfluoroalkyl β-ethoxy enones **2** and derived perfluoroalkyl-containing

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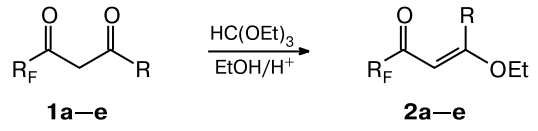
tridentate β-amino enones **3** and symmetrical and non-symmetrical tetradentate bis(β-amino enones) **4** and **5** for further investigations of their complexing properties.

Results and Discussion

Perfluoroalkyl-containing 1,3-diketones **1a—e** react with $HC(OEt)_3$ in ethanol in the presence of catalytic amounts of $HClO_4$ or H_2SO_4 to give β-ethoxy enones **2a—e** (Scheme 1; Tables 1, 2). The use of other catalysts (TsOH, HCl, and H_3PO_4) was ineffective.

Scheme 1



	a	b	c	d	e
R_F	CF_3	C_4F_9	C_4F_9	C_4F_9	C_6F_{13}
R	Me	Me	Et	Pr^i	Et

The reaction with diketone **1d** proceeds incompletely and the final reaction mixture contains appreciable amounts of the starting diketone, which cannot be separated from the target β-ethoxy enone **2d** by distillation or chromatography. An increase in the reaction time or the amount of $HC(OEt)_3$ or the catalyst was ineffective. The use of a bulkier substituent (R = Bu^t and Ph) prevents the formation of β-ethoxy enone altogether. The reaction of trifluoroacetylacetone **1a** with $HC(OEt)_3$ gives a complex mixture of products, in which the starting 1,3-diketone (in small amounts) and β-ethoxy enone **2a** (~27%) were identified by ^{1}H NMR spectroscopy (see Table 1).

The reaction yields only one of two possible isomers, which is confirmed by the presence of one set of signals in the ^{1}H NMR spectra of compounds **2a—e** (see Table 1). The perfluoroalkyl residue is linked with the carbonyl group, which is evident from downfield shifts of the signals for the nonfluorinated terminal alkyl substituents R (compared to the respective signals for the starting diketones **1a—e**, $\Delta\delta$ = 0.18—1.53 ppm) because of the deshielding effect of the double bond. The chemical shifts for the olefinic protons and the substituents R in *E*-trifluoromethyl β-methoxy enones[16,18] are similar to those in the ^{1}H NMR spectra of compounds **2a—e**, which allows assignment of the *E*-configuration to them.

Perfluoroalkyl β-ethoxy enones **2b,e**, as well as β-ethoxyvinyl and β-methoxypropenyl trifluoromethyl ketones (**2f**) and (**2g**) (see Ref. 16), successfully react with PDA. We found that at the 1 : 1 ratio of the reagents, the reaction in chloroform is completed in 5—10 min to give β-amino enones **3a—d** (Scheme 2; see Tables 2, 3).

Reactions of β-alkoxy enones with PDA in the ratio 2 : 1 in chloroform proceed smoothly only with com-

Table 1. Yields and physical and spectroscopic characteristics of perfluoroalkyl-containing β-ethoxy enones **2**

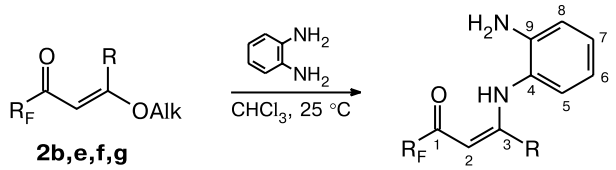
Compound	R	R_F	Yield (%)	B.p. /°C (*p*/Torr)	^{1}H NMR ($CDCl_3$, δ, *J*/Hz)	IR[a], ν/cm^{-1}
4-Ethoxy-1,1,1-trifluoropent-3-en-2-one (**2a**)[b]	Me	CF_3	27[c]	—	1.42 (t, 3 H, $OCH_2C\underline{H}_3$, ^3J = 7.0); 2.41 (s, 3 H, CH_3); 4.01 (q, 2 H, $OC\underline{H}_2CH_3$, ^3J = 7.0); 5.66 (s, 1 H, =CH)	—
2-Ethoxy-5,5,6,6,7,7,8,8,8-nonafluorooct-2-en-4-one (**2b**)	Me	C_4F_9	72	79—81 (27)	1.41 (t, 3 H, $OCH_2C\underline{H}_3$, ^3J = 7.1); 2.41 (s, 3 H, CH_3); 4.01 (q, 2 H, $OC\underline{H}_2CH_3$, ^3J = 7.1); 5.73 (s, 1 H, =CH)	3122, 1699, 1575
3-Ethoxy-6,6,7,7,8,8,9,9,9-nonafluorononon-3-en-5-one (**2c**)	Et	C_4F_9	68	100—115 (30)	1.14 (t, 3 H, $CH_2C\underline{H}_3$, ^3J = 7.5); 1.42 (t, 3 H, $OCH_2C\underline{H}_3$, ^3J = 7.0); 2.82 (q, 2 H, $C\underline{H}_2CH_3$, ^3J = 7.5); 4.00 (q, 2 H, $OC\underline{H}_2CH_3$, ^3J = 7.0); 5.67 (s, 1 H, =CH)	3122, 1697, 1572
3-Ethoxy-6,6,7,7,8,8,9,9,9-nonafluoro-2-methylnon-3-en-5-one (**2d**)[b]	Pr^i	C_4F_9	23[c]	—	1.11 (d, 6 H, $CH(C\underline{H}_3)_2$, ^3J = 6.9); 1.41 (t, 3 H, $OCH_2C\underline{H}_3$, ^3J = 7.0); 3.92 (sept, 1 H, $C\underline{H}(CH_3)_2$, ^3J = 6.9); 3.99 (q, 2 H, $OCH_2C\underline{H}_3$, ^3J = 7.0); 5.60 (s, 1 H, =CH)	—
3-Ethoxy-6,6,7,7,8,8,9,9,10,10,11,11,11-tridecafluoroundec-3-en-5-one (**2e**)	Et	C_6F_{13}	75	70—75 (17)	1.15 (t, 3 H, $CH_2C\underline{H}_3$, ^3J = 7.5); 1.42 (t, 3 H, $OCH_2C\underline{H}_3$, ^3J = 7.0); 2.82 (q, 2 H, $C\underline{H}_2CH_3$, ^3J = 7.5); 4.00 (q, 2 H, $OC\underline{H}_2CH_3$, ^3J = 7.0); 5.67 (s, 1 H, =CH)	3117, 1698, 1574

[a] Thin film.
[b] The compounds were identified from ^{1}H NMR data.
[c] The yield from ^{1}H NMR data.

Table 2. Elemental analysis data for compounds **2—5**

Compound	Found / Calculated (%)				Molecular formula
	C	H	N	F	
2b	36.02 / 36.16	2.68 / 2.73	—	51.84 / 51.48	$C_{10}H_9F_9O_2$
2c	37.95 / 38.16	3.11 / 3.20	—	49.47 / 49.39	$C_{11}H_{11}F_9O_2$
2e	34.91 / 34.99	2.61 / 2.49	—	55.34 / 55.35	$C_{13}H_{11}F_{13}O_2$
3a	52.37 / 52.18	4.03 / 3.94	12.25 / 12.17	24.93 / 24.76	$C_{10}H_9N_2F_3O$
3b	54.26 / 54.10	4.36 / 4.54	11.47 / 11.61	23.30 / 23.34	$C_{11}H_{11}N_2F_3O$
3c	42.51 / 42.65	2.84 / 2.81	6.93 / 7.11	43.49 / 43.37	$C_{14}H_{11}N_2F_9O$
3d	40.39 / 40.17	2.67 / 2.58	5.43 / 5.51	48.25 / 48.59	$C_{17}H_{13}N_2F_{13}O$
4a	47.57 / 47.74	2.81 / 2.87	7.87 / 7.95	32.54 / 32.36	$C_{14}H_{10}N_2F_6O_2$
4b	50.48 / 50.53	3.67 / 3.71	7.31 / 7.37	30.04 / 29.97	$C_{16}H_{14}N_2F_6O_2$
4c	38.81 / 38.84	2.06 / 2.07	4.22 / 4.12	50.30 / 50.27	$C_{22}H_{14}N_2F_{18}O_2$
4d	40.55 / 40.69	2.57 / 2.56	3.68 / 3.95	48.09 / 48.27	$C_{24}H_{18}N_2F_{18}O_2$
4e	37.22 / 37.02	1.93 / 2.00	3.06 / 3.08	54.27 / 54.38	$C_{28}H_{18}N_2F_{26}O_2$
5a	49.19 / 49.19	3.38 / 3.30	7.75 / 7.65	31.03 / 31.12	$C_{15}H_{12}N_2F_6O_2$
5b	43.20 / 43.03	2.53 / 2.66	5.30 / 5.28	43.15 / 42.99	$C_{19}H_{14}N_2F_{12}O_2$
5c	44.29 / 44.13	2.60 / 2.96	5.17 / 5.15	42.04 / 41.88	$C_{20}H_{16}N_2F_{12}O_2$

Scheme 2



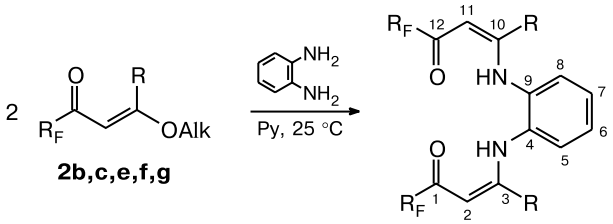
2b,e,f,g **3a—d** (82—97%)

2	**3**	R_F	R
f	**a**	CF_3	H
g	**b**	CF_3	Me
b	**c**	C_4F_9	Me
e	**d**	C_6F_{13}	Et

Alk = Et (**2b,e,f**), Me (**2g**)

pound **2f**, yielding the known bis(β-amino enone) **4a**.[14] The formation of bis(β-amino enones) **4b,c** from β-alkoxy enones **2g,b** requires a threefold excess of the latter and takes from 3 to 4 days. In the case of bulkier terminal alkyl substituents (compounds **2c,e**), the reaction is not completed even in a week. However, replacement of chloroform by pyridine allowed us to obtain symmetrical bis(β-amino enones) **4a—e** in high yields in one to two days from all the starting perfluoroalkyl-containing β-alkoxy enones at the stoichiometric ratio of the reagents (Scheme 3; see Tables 2, 3).

Scheme 3

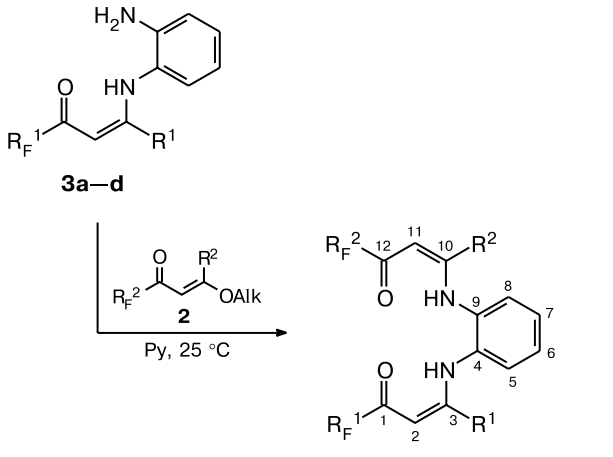


2b,c,e,f,g **4a—e** (83—96%)

2	**f**	**g**	**b**	**c**	**e**
4	**a**	**b**	**c**	**d**	**e**
R_F	CF_3	CF_3	C_4F_9	C_4F_9	C_6F_{13}
R	H	Me	Me	Et	Et

Reactions of β-amino enones **3a—c** with β-alkoxy enones (in the ratio 1 : 1) in pyridine afford both symmetrical (**4b,c,e**) and nonsymmetrical bis(β-amino enones) (**5a—c**) in high yields (Scheme 4; see Tables 2, 3).

Scheme 4



Compounds	R_F^1	R_F^2	R^1	R^2
2g, **3b**, **4b**	CF_3	CF_3	Me	Me
2b, **3c**, **4c**	C_4F_9	C_4F_9	Me	Me
2a, **3d**, **4e**	C_6F_{13}	C_6F_{13}	Et	Et
2f, **3b**, **5a**	CF_3	CF_3	Me	H
2g, **3a**, **5a**	CF_3	CF_3	H	Me
2b, **3b**, **5b**	CF_3	C_4F_9	Me	Me
2g, **3c**, **5b**	C_4F_9	CF_3	Me	Me
2c, **3b**, **5c**	CF_3	C_4F_9	Me	Et

Table 3. Yields, melting points, and IR spectra of perfluoroalkyl-containing mono- and bis(β-amino enones) **3—5**

Compound	R^1	R^2	R_F^1	R_F^2	Yield (%)	M.p. /°C	IR[a], ν/cm^{-1}
2-(2-Trifluoroacetylvinyl-amino)aniline (**3a**)	H	—	CF_3	—	82	99—101	3443, 3365, 3234, 3148 1673, 1628, 1596, 1562, 1512, 1463
2-(1-Methyl-2-trifluoroacetyl-vinylamino)aniline (**3b**)	Me	—	CF_3	—	83	96—97	3451, 3350, 3222, 3239 1624, 1602, 1587, 1571, 1555
2-(1-Methyl-2-perfluoropentanoyl-vinylamino)aniline (**3c**)	Me	—	C_4F_9	—	97	46—47	3468, 3371, 3217, 3071, 3041, 1615, 1576, 1548
2-(1-Ethyl-2-perfluoroheptanoyl-vinylamino)aniline (**3d**)	Et	—	C_6F_{13}	—	97	60—61	3469, 3378, 3196, 1628, 1607, 1571
1,2-Bis(2-trifluoroacetylvinyl-amino)benzene (**4a**)	H	H	CF_3	CF_3	83	147—148	3197, 3117, 3062, 1645, 1606, 1574, 1506
1,2-Bis(1-methyl-2-trifluoroacetyl-vinylamino)benzene (**4b**)	Me	Me	CF_3	CF_3	86 (90)[b]	122—123	3454, 3097, 1612, 1575, 1515
1,2-Bis(1-methyl-2-perfluoropenta-noylvinylamino)benzene (**4c**)	Me	Me	C_4F_9	C_4F_9	92 (94)[b]	110—111	3471, 3126, 1617, 1584, 1520
1,2-Bis(1-ethyl-2-perfluoropentanoyl-vinylamino)benzene (**4d**)	Et	Et	C_4F_9	C_4F_9	90	42—43	3450, 3118, 1601, 1582, 1511
1,2-Bis(1-ethyl-2-perfluoroheptanoyl-vinylamino)benzene (**4e**)	Et	Et	C_6F_{13}	C_6F_{13}	96 (92)[b]	44—46	3455, 3117, 1601, 1581, 1566, 1513
2-(1-Methyl-2-trifluoroacetylvinyl-amino)-1-(2-trifluoroacetylvinyl-amino)benzene (**5a**)	H	Me	CF_3	CF_3	77 (62)[c]	119—120	3450, 3132, 1650, 1621, 1617, 1595, 1564, 1513
2-(1-Methyl-2-perfluoropentanoylvinyl-amino)-1-(1-methyl-2-trifluoroacetyl-vinylamino)benzene (**5b**)	Me	Me	CF_3	C_4F_9	97 (94)[d]	53	3461, 3112, 2986, 2940, 1615, 1598, 1578, 1518
2-(1-Ethyl-2-perfluoropentanoylvinyl-amino)-1-(1-methyl-2-trifluoroacetyl-vinylamino)benzene (**5c**)	Me	Et	CF_3	C_4F_9	95	—	3451, 3123, 1618, 1601, 1584, 1520

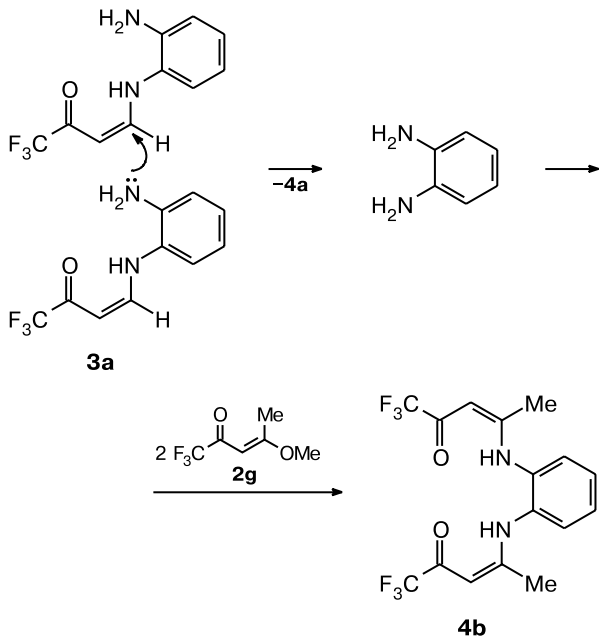
[a] Nujol.
[b] The yield from the reaction of β-amino enone with β-alkoxy enone is given in parentheses.
[c] The yield from the reaction of compound **3a** with compound **2g** is given in parentheses.
[d] The yield from the reaction of compound **3c** with compound **2g** is given in parentheses.

Compound **5a** is the exception. In this case, the choice of the starting β-amino and β-alkoxy enones affects not only the yield, but also the purity of the product. For instance, the reaction of compound **3a** with compound **2g** gives nonsymmetrical bis(β-amino enone) **5a** in 62% yield and symmetrical bis(β-amino enones) **4a** (~8%) and **4b** (~5%). Apparently, this is due to a competitive transamination of compound **3a** followed by a reaction of the liberated PDA with β-methoxy enone **2g** (Scheme 5).

The reaction of compound **3b** with compound **2f** affords product **5a** in a higher yield (77%) and the final mixture contains no other bis(β-amino enones). Such an influence of the nature of the starting reagent can be probably associated with the steric effects of terminal substituents R. Indeed, the ^{1}H NMR spectrum of β-amino enone **3a** treated with pyridine for one day and dried *in vacuo* revealed the presence of bis(β-amino enone) **4a** (~16%); in the case of β-amino enone **3b**, the formation of compound **4b** was not observed.

The ^{1}H NMR spectra of compounds **3a—d**, **4a—e**, and **5a—c** (Table 4) show characteristic signals for olefinic protons at δ 5.58—5.72 and NH protons involved in strong intramolecular hydrogen bonding (δ 11.70—12.60), which agrees with data for perfluoroalkyl *N*-aryl-β-amino enones.[23] In addition, the ^{1}H NMR spectra of compounds **3a—d** contain broadened singlets for a free amino group (δ 3.71—3.80, 2 H). The *Z*-configuration of the double bond in bis(β-amino enone) **4a** has been deduced earlier from the coupling constant between the terminal and olefinic protons (J = 7.6 Hz).[14] The *Z*-configuration of the double bond in mono- and bis(β-amino enones) **3a** and **5a** containing a fragment of trifluoromethyl vinyl ketone was proved analogously (J = 7.4 and 7.6 Hz). The ^{1}H NMR spectra of compounds **3a**, **4a**, and **5a** suggest a spin-spin coupling between the terminal and chelated protons (J = 12.3—13.0 Hz), owing to which signals for the NH protons in bis(β-amino enones) **4a** and **5a** appear as doublets. However, the corresponding signal for mono-β-amino enone **3a** appears as a broadened singlet, probably because of a faster proton exchange. The ^{19}F and ^{13}C NMR spectra of compounds **3a,b**, **4a,b**, and **5a** (Table 5) also confirm the above assignments.

Scheme 5



It should be noted that the ^{1}H chemical shifts for the aryl substituent in compounds **3a**, **4a**, and **5a** (R= H) differ from those in amino enones (R= Alk) (see Table 4). Indeed, the protons of the aryl group in compound **3a** appear as a pair of multiplets at δ 6.80—6.88 and 7.05—7.11 (2 H each), while the ^{1}H NMR spectra of amino enones **3b—d** show a set of multiplets at δ 6.75—6.81, 6.99—7.01, and 7.14—7.19 with an integral intensity ratio of 2 : 1 : 1, respectively. The signals for the components of the AA´BB´ system of the aryl substituent in symmetrical bis(β-amino enones) **4b—e** are shifted downfield compared to those for compound **6a** ($\Delta\delta_{(5,8)}$ = 0.12—0.14 ppm; $\Delta\delta_{(6,7)}$ = 0.06—0.08 ppm). In the case of nonsymmetrical bis(β-amino enones), the protons of the *o*-phenylene fragment appear as one two-proton and two one-proton multiplets for compound **5a** and as a pair of two-proton multiplets for compounds **5b,c**. The deshielding effect of the β-amino enone fragment with R = Me on the ^{13}C chemical shifts in the aryl substituent is stronger in compounds **3a,b**, **4a,b**, and **7a** (see Table 5). Apparently, these differences are due to the fact that the trifluoromethyl vinyl ketone fragment in amino enones **3a**, **4a**, and **5a** can be coplanar (or nearly coplanar) with the aromatic ring, which favors conjugation of the lone electron pair of the enamine N atoms with the π-electrons of the benzene ring. In other amino enones, this is precluded by steric interactions between the terminal alkyl substituents and the H(5) and H(8) protons.

Thus, we studied the reactions of perfluoroalkyl-containing 1,3-diketones with triethyl orthoformate, which afforded a number of perfluoroalkyl β-ethoxy enones. Subsequent reactions of the latter with *o*-phenylenediamine

Table 4. ^{1}H NMR spectra of perfluoroalkyl-containing mono- and bis(β-amino enones) **3—5** ($CDCl_3$, δ, *J*/Hz)

Compound	H(2), H(11)	R	Ar	NH	NH_2 (br.s, 2 H)
3a	5.69 (dq, 1 H, $^3J_{H,H}$ = 7.3, $^4J_{H,F}$ = 0.5)	7.60 (dd, 1 H, H(3), ^3J = 13.0, ^3J = 7.3)	6.80—6.88 (m, 2 H, H(6), H(7)); 7.05—7.11 (m, 2 H, H(5), H(8))	11.79 (br.s, 1 H)	3.71
3b	5.58 (s, 1 H)	2.01 (s, 3 H, CH_3)	6.76—6.81 (m, 2 H, H(6), H(7)); 6.99—7.01 (m, 1 H, H(8)); 7.14—7.19 (m, 1 H, H(5))	12.03 (br.s, 1 H)	3.80
3c	5.62 (t, 1 H, $^4J_{H,F}$ = 1.4)	2.02 (s, 3 H, CH_3)	6.75—6.81 (m, 2 H, H(6), H(7)); 6.99—7.01 (m, 1 H, H(8)); 7.14—7.19 (m, 1 H, H(5))	12.11 (br.s, 1 H)	3.78
3d	5.65 (t, 1 H, $^4J_{H,F}$ = 1.4)	1.10 (t, 3 H, $CH_2C\underline{H}_3$, ^3J = 7.6); 2.31 (q, 2 H, $C\underline{H}_2CH_3$, ^3J = 7.6)	6.75—6.81 (m, 2 H, H(6), H(7)); 6.99—7.01 (m, 1 H, H(8)); 7.15—7.19 (m, 1 H, H(5))	12.12 (br.s, 1 H)	3.78
4a	5.76 (dq, 2 H, $^3J_{H,H}$ = 7.6, $^4J_{H,F}$ = 0.4)	7.52 (dd, 2 H, H(3), H(10), ^3J = 12.4, ^3J = 7.6)	7.25, 7.30 (AA´BB´ system, 4 H, H(5), H(8) and H(6), H(7), $^3J_{5,6}$ = 8.3, $^4J_{5,7}$ = 1.4, $^3J_{6,7}$ = 6.7)	11.70 (d, 2 H, ^3J = 12.4)	—
4b	5.61 (s, 2 H)	2.07 (s, 6 H, 2 CH_3)	7.31, 7.42 (AA´BB´ system, 4 H, H(5), H(8) and H(6), H(7), $^3J_{5,6}$ = 8.3, $^4J_{5,7}$ = 1.3, $^3J_{6,7}$ = 7.2)	12.34 (br.s, 2 H)	—
4c	5.64 (t, 2 H, $^4J_{H,F}$ = 1.2)	2.06 (s, 6 H, 2 CH_3)	7.32, 7.43 (AA´BB´ system, 4 H, H(5), H(8) and H(6), H(7), $^3J_{5,6}$ = 8.2, $^4J_{5,7}$ = 1.4, $^3J_{6,7}$= 7.3)	12.48 (br.s, 2 H)	—

(*to be continued*)

Table 4 (*continued*)

Compound	H(2), H(11)	R	Ar	NH	NH_2 (br.s, 2 H)
4d	5.64 (t, 2 H, $^4J_{H,F}$ = 1.2)	1.12 (t, 6 H, 2 $CH_2C\underline{H}_3$, ^3J = 7.5); 2.29 (q, 4 H, 2 $C\underline{H}_2CH_3$, ^3J = 7.5)	7.32, 7.43 (AA´BB´ system, 4 H, H(5), H(8) and H(6), H(7), $^3J_{5,6}$ = 8.3, $^4J_{5,7}$ = 1.3, $^3J_{6,7}$ = 7.2)	12.44 (br.s, 2 H)	—
4e	5.64 (t, 2 H, $^4J_{H,F}$ = 1.2)	1.11 (t, 6 H, 2 $CH_2C\underline{H}_3$, ^3J = 7.5); 2.29 (q, 4 H, 2 $C\underline{H}_2CH_3$, ^3J = 7.5)	7.33, 7.44 (AA´BB´ system, 4 H, H(5), H(8) and H(6), H(7), $^3J_{5,6}$ = 8.3, $^4J_{5,7}$ = 1.3, $^3J_{6,7}$ = 7.2)	12.45 (br.s, 2 H)	—
5a	5.72 (s, 1 H, H(11)); 5.72 (d, 1 H, H(2), ^3J = 7.4)	1.97 (s, 3 H, CH_3); 7.63 (dd, 1 H, ^3J = 12.6, ^3J = 7.4, H(3))	7.22—7.24 (m, 2 H, H(6), H(7)); 7.31—7.33 (m, 1 H, H(5)); 7.41—7.46 (m, 1 H, H(8))	11.73 (d, 1 H, ^3J = 12.6); 12.14 (br.s, 1 H)	—
5b	5.59 (s, 1 H); 5.66 (t, 1 H, $^4J_{H,F}$ = 1.2)	2.06, 2.07 (both s, 3 H each, CH_3)	7.29—7.34 (m, 2 H, H(6), H(7)); 7.40—7.45 (m, 2 H, H(5), H(8))	12.36, 12.47 (both br.s, 1 H each)	—
5c	5.57 (s, 1 H); 5.68 (t, 1 H, $^4J_{H,F}$ = 1.4)	1.13 (t, 3 H, $CH_2C\underline{H}_3$, ^3J = 7.5); 2.06 (s, 3 H, CH_3); 2.32 (q, 2 H, $C\underline{H}_2CH_3$, ^3J = 7.5)	7.29—7.35 (m, 2 H, H(6), H(7)); 7.39—7.46 (m, 2 H, H(5), H(8))	12.33, 12.46 (both br.s, 1 H each)	—

Table 5. ^{13}C and ^{19}F NMR spectra of selected trifluoromethyl-containing mono- and bis(β-amino enones) ($CDCl_3$, δ, $J_{C,F}(J_{H,F})$/Hz)

Compound	^{13}C NMR						^{19}F NMR
	C(1), C(12) (q)	C(2), C(11) (q)	C(3), C(10) (s)	R^1, R^2 (s)	R_F^1, R_F^2 (q)	Ar (s)	
3a	179.2 (^2J = 34.0)	90.2 (^3J = 1.2)	152.1	—	117.1 (^1J = 288.3)	117.8 (C(8)), 119.0 (C(7)), 120.2 (C(6)), 127.0 (C(9)), 127.2 (C(5)), 137.8 (C(4))	84.81 (d, ^4J = 0.5)
3b	171.0 (^2J = 33.0)	90.7 (^3J = 1.5)	170.6	19.9	117.6 (^1J = 288.5)	116.3 (C(8)), 118.7 (C(7)), 122.7 (C(9)), 127.6 (C(6)), 129.4 (C(5)), 142.4 (C(4))	85.00 (d, ^4J = 0.3)
4a	180.3 (^2J = 34.7)	92.1*	151.1	—	116.7 (^1J = 288.8)	120.43 (C(6), C(7)), 127.3 (C(5), C(8)), 131.4 (C(4), C(9))	84.69 (s)
4b	177.7 (^2J = 33.7)	91.9 (^3J = 1.7)	167.9	19.9	117.2 (^1J = 288.4)	127.5 (C(6), C(7)), 128.6 (C(5), C(8)), 133.1 (C(4), C(9))	84.76 (s)
5a	178.1 (C(12), ^2J = 33.6); 180.1 (C(1), ^2J = 34.6)	91.8 (C(2), ^3J = 1.2); 92.0 (C(11), ^3J = 1.4)	148.4 (C(3)), 169.0 (C(10))	19.9	116.7 (^1J = 288.8); 117.3 (^1J = 288.6)	116.2 (C(6)), 125.7 (C(5)), 127.0 (C(4)), 129.0 (C(7)), 129.9 (C(8)), 135.8 (C(9))	84.58 (s); 84.90 (d, ^4J = 0.8)

* Singlet.

gave a number of novel perfluoroalkyl-containing tridentate β-amino enones and symmetrical and nonsymmetrical tetradentate bis(β-amino enones). We demonstrated that the rate and selectivity of formation of bis(β-amino enones) are affected by the nonfluorinated terminal substituent in perfluoroalkyl β-ethoxy enones.

Experimental

Commercial β-ethoxyvinyl trifluoromethyl ketone (**2f**) (Aldrich) was used. β-Methoxy enone **2g** was prepared according to a known procedure.[16] 1,3-Diketones **1a—e** were prepared as described earlier.[24] Ethanol was dried over zeolite (3Å); triethyl orthoformate was purified by distillation (b.p. 144—146 °C); pyridine was dried with NaOH and distilled. *o*-Phenylenediamine was twice recrystallized from ethanol.

^1H, ^{19}F, and ^{13}C NMR spectra were recorded on a Bruker DRX-400 spectrometer (400.13, 380, and 100.61 MHz, respectively) in $CDCl_3$ with Me_4Si as the internal standard. IR spectra were recorded on a Spectrum One FTIR spectrophotometer in a thin film and Nujol. The course of the reactions was monitored by TLC on Silufol UV-254 plates with $CHCl_3$ as the eluent; spots were visualized with a saturated aqueous solution of $Cu(OAc)_2$.

Reactions of perfluoroalkyl-containing 1,3-diketones 1a—e with triethyl orthoformate (general procedure). A 70% solution of $HClO_4$ (50 μL) was added to a solution of 1,3-diketone (0.05 mol) and triethyl orthoformate (0.052 mol) in dry EtOH (10 mL). The reaction mixture was refluxed for 3 to 5 h and then

stirred with a water—hexane mixture (1 : 1, 50 mL) for 20 min. The aqueous layer was separated and washed with hexane (3×10 mL). The organic extracts were combined, dried with Na_2SO_4, and distilled to give compounds **2a—e**. The yields and characteristics of compounds **2a—e** are given in Tables 1 and 2.

Synthesis of β-amino enones 3a—d (general procedure). A solution of the corresponding β-alkoxy enone (1 mmol) in $CHCl_3$ (2 mL) was added to a solution of PDA (1 mmol) in $CHCl_3$ (5 mL). The reaction mixture was kept for 5 to 10 min and passed through a column with silica gel (70—230, 3 cm). The silica gel was washed with $CHCl_3$ (6×10 mL) and the eluate was concentrated. The yields and characteristics of compounds **3a—d** are given in Tables 2—5.

Synthesis of bis(β-amino enones) 4a—e (general procedure). The corresponding β-alkoxy enone (1 mmol) was added to a solution of PDA (0.5 mmol) in pyridine (3 mL). The reaction mixture was stirred for 1—2 days and concentrated *in vacuo*. The residue was dissolved in $CHCl_3$ (10 mL), stirred with oxalic acid (0.5 mmol) for 20 min, and filtered through a layer of silica gel (70—230, 1 cm). The silica gel was washed with $CHCl_3$ (4×10 mL) and the eluate was concentrated. The yields and characteristics of compounds **4a—e** are given in Tables 2—5.

Synthesis of bis(β-amino enones) 5a—c (general procedure). The corresponding β-alkoxy enone **2** (0.1 mmol) was added to a solution of β-amino enone (0.1 mmol) in pyridine (2 mL). The reaction mixture was stirred for 1—2 days and then treated as described above. The yields and characteristics of compounds **5a—c** are given in Tables 2—5.

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