Condensation of fluoroalkyl-containing 1,3-dicarbonyl compounds with ethylenediamine

V. I. Saloutin, Z. E. Skryabina and Y. V. Burgart
Department of Fine Organic Synthesis, Urals Division, Russian Academy of Sciences, 620219, GSP-147 Ekaterinburg (Russia)

(Received July 10, 1991; accepted October 30, 1991)

Abstract

2,3-Dihydro-1*H*-1,4-diazepines have been prepared by the direct interaction of fluoroalkylated 1,3-diketones with ethylenediamine hydroperchlorate; similarly, 1,2,3,4-tetrahydro-1,4-diazepine-5-ones have been obtained from fluorinated 1,3-keto esters. Under mild conditions, fluorinated copper(II) 1,3-diketonates, and copper(II) and nickel(II) *N,N'*-ethylenebis(aminovinyl ketonates) were found to react with ethylenediamine to form fluoroalkyl-containing *N,N'*-ethylenebis(aminovinyl ketones) and/or 2,3-dihydro-1*H*-1,4-diazepines.

Introduction

The reaction of acetylacetone with ethylenediamine has rich synthetic possibilities, including the formation of macrocyclic complexes [1]. It is known that hexafluoroacetylacetone reacts with ethylenediamine to give a non-stable *N,N'*-ethylenebis(aminovinyl ketone), which can be converted to the corresponding 1,4-diazepine [2]. In contrast, the reaction of non-symmetrical fluoroalkyl-containing 1,3-diketones with ethylenediamine yields only the corresponding *N,N'*-ethylenebis(aminovinyl ketones) [3–5], with the exception of 1,1,1-trifluoromethyl-5,5-dimethylhexane-2,4-dione from which the 1,4-diazepine has been prepared [5]. Other 7-fluoroalkyl-1,4-diazepines have been obtained via the reaction of ethylenediamine with the 1,3-aminovinyl ketones where the amino group is attached to the carbon atom carrying with fluoroalkyl substituent [6]. In the presence of nickel(II) ions, trifluoro- and hexafluoro-acetylacetones react with ethylenediamine to form nickel(II) bis(1,3-diketonates) [7], i.e. acyclic products. The template reaction of trifluoroacetylacetone with triethylenetetraamine not only gives the chelate of the starting diketone but also the 13-membered macrocyclic complex [8].

In this paper the interaction of ethylenediamine with fluorine-containing 1,3-diketones and with the metal chelates of these 1,3-diketones and related *N,N'*-ethylenebis(aminovinyl ketones) is described.

Experimental

Melting points were measured in open capillaries and are reported uncorrected. Infrared spectra were measured on a Specord 75 IR spectrometer.

0022-1139/92/$5.00

^{1}H NMR spectra were recorded on a Tesla BS-567 A instrument (^{1}H: 100 MHz) in CD_3-$COCD_3$ using TMS as an external standard. All chemical shifts are reported in ppm and wavenumbers in cm^{-1}. Mass spectral data were obtained using a MAT-311a mass spectrometer. Column chromatography was performed on silicagel L 100/250 using methanol as the eluant. Thin-layer chromatography was performed on 'Silufol-UV-254' plates in methanol.

Materials

Ethylenediamine dihydroperchlorate was prepared by the method described previously [9]. **CAUTION: Heating this perchlorate is dangerous.**

Synthesis of 2,3-dihydro-7-fluoroalkyl-1H-1,4-diazepines monohydroperchlorates (2)

A mixture of ethylenediamine dihydroperchlorate (2.6 g, 10 mmol), anhydrous ethylenediamine (0.6 g, 10 mmol) and the corresponding fluoroalkylated 1,3-diketone (**1**) (25 mmol) was heated carefully at 100–120 °C for 8–10 h. The reaction mixture was dissolved in 20 ml of alcohol and the product obtained by precipitation through the addition of ether.

Compound **2a**: Yield, 59%; m.p., 188–190 °C. ^{1}H NMR δ: 10.05 (2H, w.s, NH); 6.60 (1H, t-t, J(H–F) = 52.3, 4.7 Hz); 5.52 (1H, s, CH); 3.97 (4H, w.s, CH_2CH_2); 2.52 (3H, s, Me) ppm. IR: 3300, 1575 (NH); 1650. 1590 sh (C=N$^+$, C=C); 1050, 620 (ClO_4^-) cm^{-1}. MS *m/e*: 210 [M $-HClO_4$]$^+$. Analysis: Found: C, 30.48; H, 3.69; Cl, 12.41; F, 24.12; N, 8.77%. Calc. for $C_8H_{10}F_4N_2 \cdot HClO_4$: C, 30.93; H, 3.57; Cl, 12.00; F, 24.46; N, 9.02%.

Compound **2b**: Yield, 51%, m.p., 145–146 °C. ^{1}H NMR δ: 10.15 (2H, w.s, NH); 7.70 (5H, m, Ph); 6.75 (1H, t-t, J(H–F) = 52.3, 4.7 Hz); 5.80 (1H, s, CH); 4.15 (4H, w.s, CH_2CH_2) ppm. IR: 3280; 1550 (NH); 1630, 1600: 1580 (C=N$^+$, C=C); 1050; 620 (ClO_4^-) cm^{-1}. Analysis: Found: C, 42.07; H, 3.31; Cl, 9.22; F, 20.44; N, 7.34%. Calc. for $C_{13}H_{12}F_4N_2 \cdot HClO_4$: C, 41.89; H, 3.52; Cl, 9.51; F, 20.39; N, 7.52%.

Compound **2c**: Yield, 71%; m.p., 154–156 °C. ^{1}H NMR δ: 10.05 (2H, w.s, NH); 6.60 (1H, t-t, J(H–F) = 52.3, 4.7 Hz); 5.60 (1H, s, CH); 3.99 (4H, w.s, CH_2CH_2); 1.43 (9H, s, Bu^t) ppm. IR: 3320, 1565 (NH); 1630; 1620 sh (C=N$^+$, C=C) cm^{-1}. Analysis: Found: C, 37.78; H, 5.10; Cl, 10.47; F, 21.46; N, 8.08%. Calc. for $C_{11}H_{16}F_4N_2 \cdot HClO_4$: C, 37.46; H, 4.86; Cl, 10.05; F, 21.55; N, 7.94%.

Compound **2d**: Yield, 68%; m.p., 151–153 °C. ^{1}H NMR δ: 10.00 (2H, w.s., NH); 7.70 (5H, m. Ph); 5.90 (1H, s, CH); 4.18 (4H, w.s, CH_2CH_2) ppm. IR: 3280, 1560 (NH); 1630; 1615; 1600; 1580 sh (C=N$^+$, C=C) cm^{-1}. Analysis: Found: C, 42.53; H, 3.42; Cl, 10.73; F, 16.45; N, 8.48%. Calc. for $C_{12}H_{11}F_3N_2 \cdot HClO_4$: C, 42.31; H, 3.55; Cl, 10.41; F, 16.73; N, 8.22%.

Synthesis of 7-fluoroalkyl-2,3-dihydro-1H-diazepines (3)

The compounds **3a**, **b**, **d** were obtained from the corresponding **2a**, **b**, **d** in the following ways. (a) To **2a** (2 g, 6 mmol) in 10 ml alcohol, a concentrated alcoholic solution of KOH was added until the pH value was

10–11. The precipitated $KClO_4$ was filtered off. The solvent was evaporated under reduced pressure. Column chromatography gave 1.0 g (75%) of **3a** as an oil. ^1H NMR δ: 6.59 (1H, t-t, J(H–F) = 53.29, 5.86 Hz); 5.05 (1H, s, CH); 3.88 (2H, m, $CH_2N{=}C$); 3.38 (2H, m, $CH_2N{-}C$); 2.06 (3H, s, Me) ppm. IR: 3240, 3100, 1535 sh (NH); 1610. 1570 (C=N, C=C) cm^{-1}. Analysis: Found: C, 45.74; H, 4.82; F, 35.98; N, 12.86%. Calc. for $C_8H_{10}F_4N_2$: C, 45.72; H, 4.80; F, 36.16; N, 13.33%. (b) To compounds **2b**, **d** (1 mmol) in water (10 ml), a concentrated aqueous solution of NaOH was added until the pH value was 10–11. The crystallized product was filtered and recrystallized from a mixture of alcohol and water to give 0.95 mmol of **3b**, **d**.

Compound **3b**: M.p., 118–119 °C. MS *m/e*: 272 [M^+]. Analysis: Found: C, 56.91; H, 4.46; F, 28.10; N, 10.27%. Calc. for $C_{13}H_{12}F_4N_2$: C, 57.35; H, 4.44; F, 27.92; N, 10.29%. The ^1H NMR and IR spectra were identical to those previously reported [6].

Compound **3d**: M.p., 147–148 °C. MS *m/e*: 240 [M^+]. Analysis: Found: C, 60.10; H, 4.89; F, 23.54; N, 11.57%. Calc. for $C_{12}H_{11}F_3N_2$: C, 60.00; H, 4.62; F, 23.72; N, 11.66%. The ^1H NMR and IR spectra were identical to those previously reported [6].

*Preparation of compounds **3e**, **f***

A mixture of ethylenediamine dihydroperchlorate (2.6 g, 10 mmol), anhydrous ethylenediamine (0.6 g, 10 mmol) and **2e**, **f** (25 mmol) was heated at 100–120 °C for 8–10 h. The reaction mixture was dissolved in alcohol. Concentrated alcoholic KOH solution was added until the pH value was 10–11. The precipitated $KClO_4$ was filtered off. The solvent was removed under reduced pressure. The residue was extracted with hot hexane and subsequent recrystallization from hexane gave **3e**, **f**.

Compound **3e**: Yield, 76%; m.p. 116–117 °C. Analysis: Found: C, 47.50; H, 5.11; F, 31.80; N, 16.00%. Calc. for $C_7H_9F_3N_2$: C, 47.19; H, 5.09; F, 31.99; N, 15.73%. The ^1H NMR and IR spectra were identical to those previously reported [6].

Compound **3f**: Yield, 85%; m.p., 109–110 °C. ^1H NMR δ: 6.70 (1H, w.s, NH); 5.35 (1H, s, CH); 3.80 (4H, m, CH_2CH_2) ppm. Analysis: Found: C, 36.09; H, 2.82; F, 49.04; N, 12.47%. Calc. for $C_7H_6F_6N_2$: C, 36.22; H, 2.60; F, 49.11; N, 12.07%. The IR spectrum was identical to that previously reported [2].

*Synthesis of 1,2,3,4-tetrahydro-7-trifluoromethyl-1,4-diazepine-5-one (**5a**)*

A mixture of ethylenediamine dihydroperchlorate (2.6 g, 10 mmol), anhydrous ethylenediamine (0.6 g, 10 mmol) and **4a** (4.6 g, 25 mmol) was heated at 100–120 °C for 8–10 h. The reaction mixture was dissolved in alcohol, treated with concentrated alcoholic KOH solution and the precipitated $KClO_4$ filtered off. Removal of the solvent gave **5a** as light yellow crystals. After recrystallization from methanol, 2.1 g (58%) of **5a** (m.p., 191–192 °C) was obtained. IR: 3280, 3170, 1560 (NH); 1650 (C=O); 1620 (C=C) cm^{-1}.

Analysis: Found: C, 40.51; H, 3.90; F, 31.67; N, 15.28%. Calc. for $C_6H_7F_3N_2O$: C, 40.09; H, 3.92; F, 31.64; N, 15.52%. The ^1H NMR spectrum was identical to that previously reported [10].

*Synthesis of 7-octafluorobutyl-1,2,3,4-tetrahydro-1,4-diazepine-5-one (**5b**)*

A mixture of **4b** (7.1 g, 25 mmol), ethylenediamine dihydroperchlorate (2.6 g, 10 mmol) and ethylenediamine (0.6 g, 10 mmol) was heated to give 4.9 g of **5b** (yield, 78%; m.p., 165–166 °C, ^1H NMR δ: 7.50 (1H, w.s, NH); 6.90 (1H, w.s, NH); 6.77 (1H, t-t, J(H–F)=51.18, 5.63 Hz); 4.89 (1H, s, CH); 3.51 (2H, m, CH_2); 3.58 (2H, m, CH_2) ppm. IR: 3250, 3180, 1560 (NH); 1640 (C=O); 1620 sh (C=C) cm^{-1}. Analysis: Found: C, 34.52; H, 2.49; F, 48.60; N, 8.73%. Calc. for $C_9H_8F_8N_2O$: C, 34.63; H, 2.58; F, 48.69; N, 8.73%.

*Reaction of bis(1,1,1-trifluoro-2,4-pentanedionato)copper(II) (**6e**) with ethylenediamine*

A solution of **6e** (1.85 g, 5 mmol) in 30 ml of $CHCl_3$ was added to anhydrous ethylenediamine (3.0 g, 50 mmol). The mixture was refluxed for 2 h. After the reaction two layers were obtained; a lower colourless chloroform layer and an upper violet coloured layer containing a mixture of $[Cu(en)_2]^{2+}$, water from the reaction and ethylenediamine. The lower chloroform layer was removed and the upper layer washed twice with chloroform. The chloroform layers were added together and the solvent removed *in vacuo*. The residue was recrystallized from methanol to give 0.1 g of **8e** (yield, 6%; m.p., 154–156 °C). (The melting point was identical to that reported in ref. 11.) IR: 3350, 1580 (NH); 1620 (C=O); 1550 (C=C) cm^{-1}. Analysis: Found: C, 43.20; H, 4.03; F, 34.69, N, 8.36%. Calc. for $C_{12}H_{14}F_6N_2O_2$: C, 43.38; H, 4.25; F, 34.31; N, 8.43%.

Removal of methanol and extraction of the residue with hot hexane gave 1.2 g of **3e** (yield, 56%; m.p., 116–117 °C). Analysis: Found: C, 47.20; H, 5.15; F, 32.02; N 15.63%. Calc. for $C_7H_9F_3N_2$: C, 47.19; H, 5.05; F, 31.99; N, 15.73%. The physicochemical constants were identical to those previously reported [6].

A mixture of **6e** (1.85 g, 5 mmol), ethylenediamine dihydroperchlorate (6.5 g, 25 mmol) and anhydrous ethylenediamine (1.5 g, 25 mmol) was refluxed in chloroform for 2 h to give **8e** (0.3 g; yield, 17%) and **3e** (0.8 g; yield, 48%).

*Reaction of bis(1,1,2,2-tetrafluoro-3,5-hexcanedionato)copper(II) (**6a**) with ethylenediamine*

A mixture of **6a** (5 g, 11.5 mmol) and anhydrous ethylenediamine (6.93 g, 115 mmol) was refluxed in chloroform for 2 h. The chloroform layer was separated and after removal of solvent the residue was extracted with hot CCl_4; **8a** (1.5 g) was obtained in 33% yield (m.p., 96–98 °C). Analysis: Found: C, 42.57; H, 4.12; F, 37.86; N, 7.10%. Calc. for $C_{14}H_{10}F_4N_2O_2$:

C, 42.43; H, 4.07; F, 38.35; N, 7.07%. The physicochemical data were identical to those previously reported [4].

On storing **6a** (5 g, 11.5 mmol) and anhydrous ethylenediamine (6.93 g, 115 mmol) for 24 h at 20 °C, 0.68 g (yield, 15%) of **8a** was obtained.

Refluxing **6a** (2.3 g, 5 mmol), ethylenediamine dihydroperchlorate (3.5 g, 25 mmol) and anhydrous ethylenediamine (1.5 g, 25 mmol) in chloroform for 2 h gave 3.2 g of **8a** (yield, 70%).

*Reaction of bis(1,1,2,2-tetrafluoro-5-phenyl-3,5-pentanedionato)copper(II) (**6b**) with ethylenediamine*

On mixing **6b** (2.8 g, 5 mmol) with anhydrous ethylenediamine (3 g, 50 mmol) in 30 ml of chloroform, a pink precipitate of **7b** was obtained. The precipitate was filtered, washed with benzene and dried *in vacuo* to give 1.8 g (yield, 53% of 7b m.p., 148 °C decomp.). Analysis: Found: C, 45.90; H, 4.28; F, 22.40; N, 8.22%. Calc. for $C_{26}H_{30}F_8N_4O_4Cu$: C, 46.05; H, 4.46; F, 22.41; N, 8.26%. IR: 3240, 3110, 1580 (NH); 1620 (C=O); 1530 (C=C) cm^{-1}. After refluxing for 2 h in chloroform, **7b** disappeared, the chloroform layer turned colourless and the lower layer was separated. After removal of solvent from the residue using column chromatography, 0.4 g (yield, 67%) of acetophenone (IR spectrum) and 1.1 g (yield, 70%) *N,N'*-bis(tetrafluoropropionylamino)ethylene (**9**) were obtained.

Compound **9** (m.p., 128–129 °C) was precipitated from methanol with water. ^1H NMR δ: 3.37 (4H, w.s, CH_2): 7.37 (1H, t-t, J(H–F) = 50.45, 5.60 Hz); 9.38 (2H, w.s, NH) ppm. IR: 3300, 1540 (NH); 1685 (C=O) cm^{-1}. Analysis: Found: C, 27.77; H, 1.56; F, 59.30; N, 5.53%. Calc. for $C_{12}H_8F_{16}N_2O_2$: C, 27.92; H, 1.56; F, 58.89; N, 5.43%.

*Reaction of bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)copper(II) (**6f**) with ethylenediamine*

A mixture of **6f** (2.4 g, 5 mmol) and anhydrous ethylenediamine (3 g, 50 mmol) in chloroform was refluxed for 2 h. The lower layer was separated and the chloroform evaporated under reduced pressure. The residue was recrystallised twice from hexane to give 0.7 g of **3f** (yield, 30%; m.p., 109–110 °C). Analysis: Found: C, 36.00; H, 2.80; F, 48.81; N, 12.20%. Calc. for $C_7H_6F_6N_2$: C, 36.22; H, 2.60; F, 49.11; N, 12.07%.

From **6f** (2.4 g, 5 mmol), anhydrous ethylenediamine (2.7 g, 45 mmol) and ethylenediamine dihydroperchlorate (1.3 g, 5 mmol) **3f** (0.95 g; yield, 41%) was obtained.

Reaction of N,N'*-ethylenebis(1,1,2,2-tetrafluoro-5-aminohexene-3-onato)copper(II) (**10a**) with ethylenediamine*

A mixture of **10a** (2.3 g, 5 mmol) and anhydrous ethylenediamine (1.5 g, 25 mmol) was refluxed in chloroform for 2 h. The lower layer was separated, while the upper layer (a mixture of $[Cu(en)_2]^{2+}$, ethylenediamine and water) was washed twice with 20 ml of chloroform. The chloroform layers were combined and after evaporation of the solvent, the residue was

dissolved in a minimum amount of methanol. Precipitation from methanol with water gave 0.46 g of **8a** (yield, 23%; m.p., 96–98 °C).

A mixture of **10a** (2.3 g, 5 mmol) and anhydrous ethylenediamine (1.5 g, 25 mmol) was refluxed in methanol under an atmosphere of argon for 8 h. After cooling, 30 ml water was added and 1.45 g of the starting material (**10a**) was filtered off (yield, 63%; m.p., 239–240 °C). IR: 1620 (C=O); 1525 (C=C) cm^{-1}. Analysis: Found: C, 37.12; H, 3.29; F, 33.52; N, 6.42%. Calc. for $C_{14}H_{14}F_8N_2O_2Cu$: C, 36.73; H, 3.08; F, 33.20; N, 6.12%.

The filtrate was evaporated *in vacuo* and the resultant oil washed with water and dried *in vacuo*. Column chromatography gave 0.12 g (yield, 5%) of **3a** (identified by IR).

Reaction of N,N'*-ethylenebis(1,1,1-trifluoro-4-aminopentene-2-onato)copper(II) (**10e**) with ethylenediamine*

In a similar manner, 1.98 g (5 mmol) of **10e** and 1.5 g (25 mmol) of anhydrous ethylenediamine were refluxed in chloroform for 2 h. After removal of the chloroform, recrystallization of the residue from methanol gave 0.2 g of **8e** (yield, 12%; m.p., 154–156 °C). Addition of water to the filtrate gave 1.0 g of **3e** (yield, 56%; m.p., 115–117 °C).

A mixture of **10e** (1.98 g, 5 mmol) and anhydrous ethylenediamine (1.5 g, 25 mmol) in 20 ml methanol was refluxed under an atmosphere of argon for 8 h. After cooling, 30 ml of water was added to give 1.2 g (60%) of the starting material (**10e**) [yield, 60%; m.p., 220 °C subl. (cf. with ref. 11)]. The filtrate was evaporated *in vacuo*, and the residue washed with 10 ml water to give 0.27 g of **3e** (yield, 15%; m.p., 115–117 °C).

Reaction of N,N'*-ethylenebis(1,1,1-trifluoro-4-aminopentene-2-onato)nickel(II) (**11**) with ethylenediamine*

A mixture of **11** (1.94 g, 5 mmol) and anhydrous ethylenediamine (1.5 g, 25 mmol) was refluxed in 20 ml methanol under an atmosphere of argon for 8 h. Precipitation from methanol with water gave 0.53 g of **3e** (yield, 30%; m.p., 116–117 °C). The filtrate was evaporated *in vacuo* and after column chromatography of the residue 0.68 g of the starting material (**11**) was obtained [yield, 35%; m.p., 270–271 °C (cf. with ref. 3)].

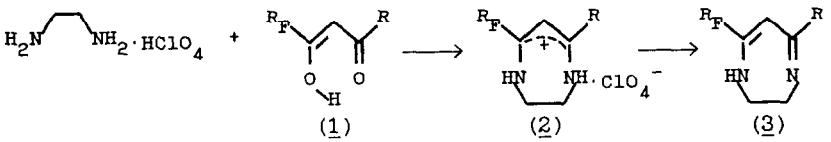
Results and discussion

Reaction of 1,3-diketones with ethylenediamine monohydroperchlorate

It is well known that acetone reacts with ethylenediamine monohydroperchlorate to give the 14-membered macrocycle [12].

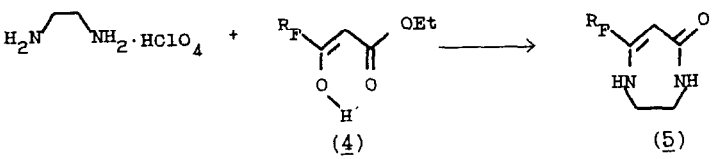
The 2,3-dihydro-1*H*-1,4-diazepines (**3**) were prepared in yields within the range 41–85% by reaction of the fluoroalkylated 1,3-diketones (**1**) with ethylenediamine monohydroperchlorate together with the intermediate isolation of 1,4-diazepine monohydroperchlorates (Scheme 1).

The salts of trifluoro- and hexafluoro-acetylacetones (**1e**) and (**1f**) could not be isolated. In these cases only the free bases were prepared. This may



Compound	R_F	R
1a, 2a, 3a	$H(CF_2)_2$	Me
1b, 2b, 3b	$H(CF_2)_2$	Ph
1c, 2c	$H(CF_2)_2$	Bu^t
1d, 2d, 3d	CF_3	Ph
1e, 3e	CF_3	Me
1f, 3f	CF_3	CF_3

Scheme 1.



Compound	R_F
4a, 5a	CF_3
4b, 5b	$H(CF_2)_4$

Scheme 2.

result from the reduced basicity of the 1,4-diazepines (**3e**) and (**3f**), arising from the electron-withdrawing effect of the CF_3 substituents. The isolation of the monoprotonated salt 2a is possibly due to the $-I$ effect of the HCF_2CF_2 group being less than that of a CF_3 group [13]. The bulky t-butyl and conjugated phenyl substituents stabilize the salts **2b–2d** and hence the free base could not be obtained from salt **2c**.

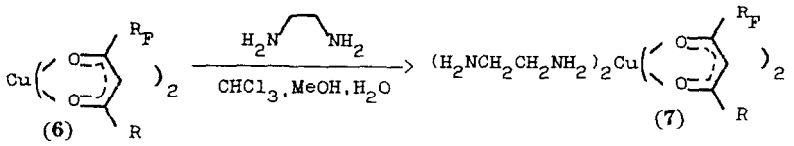
A similar reaction of fluorinated 1,3-keto esters with ethylenediamine monohydroperchlorate leads to 1,2,3,4-tetrahydro-1,4-diazepine-5-ones (**5**) (Scheme 2) similar to those produced by the reaction of trifluoroacetoacetic ester with ethylenediamine [10].

Reaction of copper(II) bis(1,3-diketonates) with ethylenediamine

Copper(II) bis(1,3-diketonates) (**6**) react with excess ethylenediamine or its salts to form adducts similar to those reported previously [2] (Scheme 3).

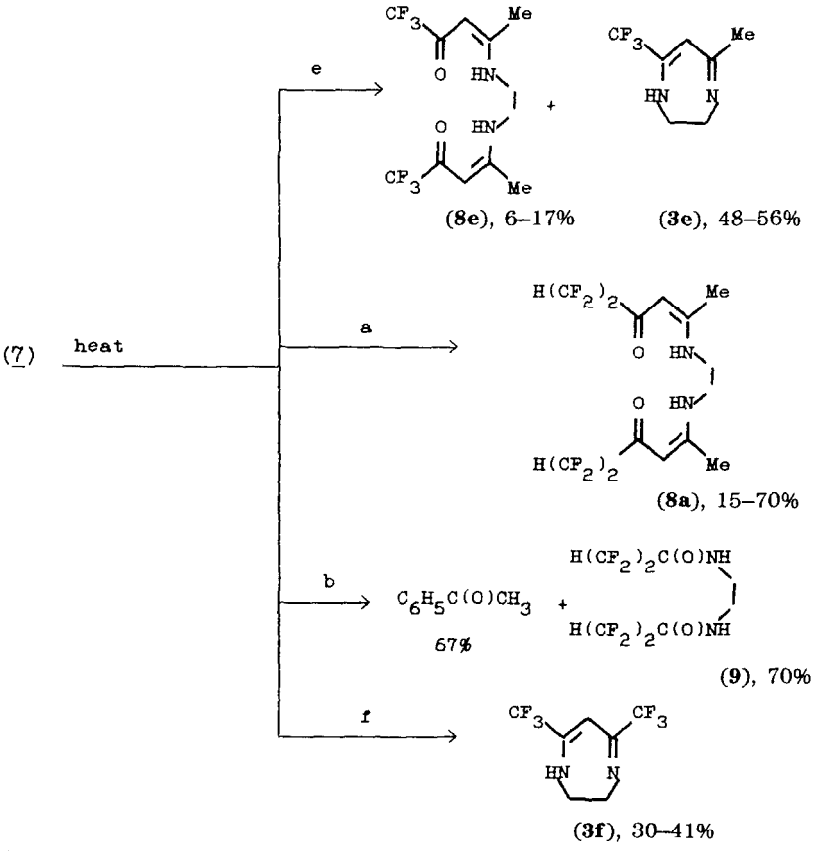
In chloroform, compounds of type **7** are unstable when stored at room temperature, and are destroyed by heat to give ethylenediamine chelates and ligands which are unlikely to react with an excess of ethylenediamine under these reaction conditions (Scheme 4).

Condensation of trifluoroacetylacetone (**1e**) and hexafluoroacetylacetone (**1f**) with ethylenediamine results in the formation of products **3e** and **3f**,



Compound	R_F	R
6a, 7a	$H(CF_2)_2$	Me
6b, 7b	CF_3	Ph
6e, 7e	CF_3	Me
6f, 7f	CF_3	CF_3

Scheme 3.



Scheme 4.

respectively, under mild reaction conditions. In the case of hexafluoroacetylacetone, the free base of the 1,4-diazepine was prepared by sublimation of the stable salt of hexafluoroacetylacetone with ethylenediamine *in vacuo* at 80–100 °C (note that heating this salt in benzene proved unsuccessful [2]).

Compound **6a** under these conditions forms the trivial product *N,N'*-ethylenebis(aminovinyl ketone) (**8a**) similar to that resulting from the reaction of 1,3-diketones with ethylenediamine [4]. The presence of the bulky aromatic substituent in compound **6b** inhibits the formation of condensation products of the latter with ethylenediamine, as found for the reaction of 1,3-diketones with ethylenediamine [5]; instead acid splitting of the diketone fragment leads to the formation of acetophenone and *N,N'*-bis(tetrafluoropropionylamino)ethylene (**9**), since the corresponding bis(1,1,2,2-tetrafluoro-5-phenyl-3,5-pentanedione)ethylenediamine is unstable. Obviously the kinetic template effect is reduced by increasing steric factors in the case of **6a** and **6b**.

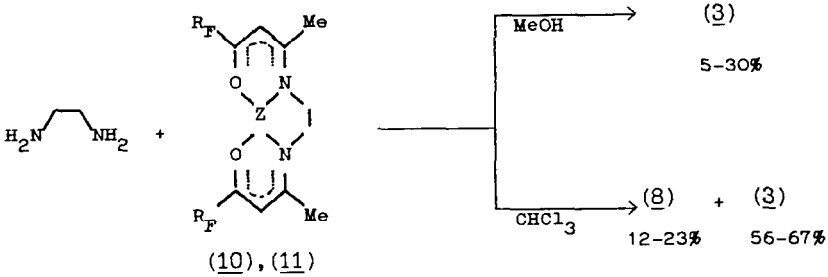
Heating **7** in water or methanol does not lead to a change of its structure.

Reaction of N,N'*-ethylenebis(aminovinyl ketones) metal chelates with ethylenediamine*

Treatment of the metal chelates of *N,N'*-ethylenebis(aminovinyl ketones) (**10** and **11**) with an excess of ethylenediamine gives *N,N'*-ethylenebis(aminovinyl ketones) (**8**) and/or 1,4-diazepines (**3**) (Scheme 5).

Methanol decreases the rate of decomposition of **10** and **11** as with compound **7**. This is probably due to the reversibility of the reaction in the presence of the soluble ethylenediamine chelate (in chloroform the insoluble cupric chelate of ethylenediamine is precipitated out of the above reaction mixture). In the reaction of **10** and **11**, the template effect of the transition metal ions is evident because the formation of 1,4-diazepines is not typical for aminovinyl ketones having an amino group at the carbon atom connected to the hydrocarbon rather than the fluoroalkyl substituent [6].

In conclusion, the reactions described demonstrate the preparation of fluoroalkyl-containing 2,3-dihydro-1*H*-1,4-diazepines from 1,3-diketones in good yield via a simple synthetic procedure.



(10), (11)

Compound	R_F	Z
3a, 8a, 10a	$H(CF_2)_2$	Cu
3e, 8e, 10e	CF_3	Cu
3e, 8e, 11	CF_3	Ni

Scheme 5.

References

1 J. P. Costes, *Polyhedron, 6* (1987) 2169.
2 M. F. Richardson and R. E. Sievers, *J. Inorg. Nucl Chem., 32* (1970) 1895.
3 S. E Livingstone and J. H. Mayfield, *Aust. J. Chem., 28* (1975) 1517.
4 K. I. Pashkevich, V. I. Saloutin, A. N. Phonin, V. V. Berenblit, V. S. Plashkin and I. Y. Postovskiy, *Zh. Vses. Khim. Ova , 26* (1981) 105.
5 S. Dilli and E Patsalides, *Aust. J Chem , 31* (1978) 765.
6 K. I. Pashkevich, A. Y Ajzikovich and I. Y. Postovskiy, *Izv. Akad. Nauk SSSR, Otd Khim. Nauk,* (1981) 455.
7 D. F. Martin and E. J Olszewski, *J. Inorg. Nucl Chem., 28* (1966) 1073
8 S. C. Cummings and R. E. Sievers, *Inorg. Chem., 9* (1970) 1131.
9 K. B. Yatzimirskiy, A. G. Kol'chinskiy, V. V. Pavlishchuk and G. G. Talanova, *Sintez makrotziklicheskikh soedineniy,* Naukova Dumka, Kiev, 1987, p. 72.
10 Q. M. J. Slusarczuk and M. M. Joullie, *J. Org Chem , 36* (1971) 37.
11 P. J. McCarthy, J. Hovey, K Veno and A. E Martell, *J. Am Chem. Soc., 77* (1955) 5820.
12 N. F. Curtis and R. W. Hay, *Chem Commun ,* (1966) 524.
13 A. N. Vereshchagin, *Induktivnyi effekt. Konstanty zamestiteley dlya korrelyatsionnogo analiza,* Nauka, Moscow, 1988, pp. 62, 63