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SYNTHESIS OF 2-PHENACYL- AND 2-(α-THENOYLMETHYL)-2-POLYFLUOROALKYLIMIDAZOLIDINES

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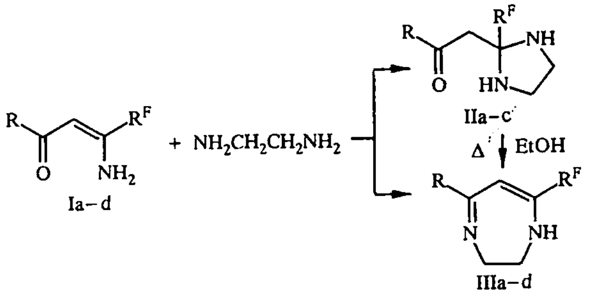
The reaction of β-amino-β-polyfluoroalkylvinylketones with ethylenediamine when boiled in alcohol or benzene leads to formation of 2,3-dihydro-1,4-diazepines, existing in the iminoenamine form and formed as a result of two nucleophilic attacks at the β-carbon atom and the carbonyl group [1]. The second possible orientation for the reaction, leading to closure of the imidazolidine ring upon double attack at the β-carbon atom with cleavage of an ammonia molecule, has not been observed in aminoenones, although formation of 2-ethoxycarbonylmethyl-2-trifluoromethylimidazolidine on reaction of ethylenediamine with ethyltrifluoroacetoacetate was reported earlier [2].

For the first time, we have established that aminoenones (Ia-c) react with ethylenediamine at room temperature without a solvent, with formation of imidazolidines (IIa-c) in almost quantitative yield, and only the aminoenone (Id) gives diazepine (IIId) under these conditions (yield, 74%). Upon boiling in alcohol for 3-6 h, the imidazolidines IIa-c are converted in 70-85% yields to the thermodynamically more stable diazepines (IIIa-c).



I–III a R = α-C_4H_3S, $R^F = CF_3$; b R = α-C_4H_3S, $R^F = (CF_2)_2H$;
c R = Ph, $R^F = CF_3$; d R = Ph, $R^F = (CF_2)_2H$

The IR spectra were taken on an IKS-29 in Vaseline oil. The PMR spectra were recorded on a Tesla BS-567A spectrometer in $CDCl_3$, working frequency 100 MHz, internal standard TMS.

2-(α-Thenoylmethyl)-2-trifluoromethylimidazolidine (IIa). Yield, 95%, mp 117-118°C (hexane). IR spectrum: 3355, 3270 (NH); 3125 (=CH); 1635 (C=O); 1515 cm^{-1} (thiophene ring). PMR spectrum: 2.71 (2H, broad s, 2NH); 3.07 (4H, s, CH_2CH_2); 3.28 (2H, s, CH_2); 7.17 (1H, dd, $J_{H4\text{-}H5} = 5.0$, $J_{H3\text{-}H4} = 3.7$ Hz, 4-H_{thioph}); 7.73 (1H, dd, $J_{H4\text{-}H5} = 5.0$, $J_{H3\text{-}H5} = 1.2$ Hz, 5-H_{thioph}); 7.77 (1H, dd, $J_{H3\text{-}H4} = 3.7$, $J_{H5\text{-}H3} = 1.2$ Hz, 3-H_{thioph}). Found, %: C 45.31; H 4.09; N 10.50. $C_{10}H_{11}F_3N_2OS$. Calculated, %: C 45.45; H 4.20; N 10.60.

2-α-Thenoylmethyl)-2-(1,1,2,2-tetrafluoroethyl)imidazolidine (IIb). Yield, 92%, mp 110-111°C (hexane). IR spectrum: 3330, 3315 (NH); 3135 (=CH); 1640 (C=O); 1520 cm^{-1} (thiophene ring). PMR spectrum: 2.79 (2H, broad s, 2NH); 2.99 (4H, s, CH_2CH_2); 3.24 (2H, s, CH_2); 6.23 (1H, tt, $^2J_{H-F} = 53.6$, $^3J_{H-F} = 6.3$ Hz, CF_2CF_2H); 7.17 (1H, dd, $J_{H4\text{-}H5} = 5.0$, $J_{H3\text{-}H4} = 3.7$ Hz, 4-H_{thioph}); 7.71 (1H, dd, $J_{H4\text{-}H5} = 5.0$, $J_{H3\text{-}H5} = 1.0$ Hz, 5-H_{thioph}); 7.77 (1H, dd, $J_{H3\text{-}H4} = 3.7$, $J_{H5\text{-}H3} = 1.0$ Hz, 3-H_{thioph}). Found, %: C 44.72; H 4.19; N 9.28. $C_{11}H_{12}F_4N_2OS$. Calculated, %: C 44.59; H 4.08; N 9.45.

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2-Phenacyl-2-trifluoromethylimidazolidine (IIc). Yield, 96%, mp 99-100°C (CCl_4). IR spectrum: 3360, 3330 (NH); 1690 (C=O); 1600, 1580 cm^{-1} (benzene ring). PMR spectrum: 2.68 (2H, broad s, 2NH); 3.06 (4H, s, CH_2CH_2); 3.36 (2H, s, CH_2); 7.40-7.63 (3H, m, 3-, 4-, and 5-H_{Ph}); 7.90-8.02 ppm (2H, m, 2- and 6-H_{Ph}). Found, %: C 55.75; H 4.94; N 10.94. $C_{12}H_{13}F_3N_2O$. Calculated, %: C 55.81; H 5.07; N 10.85.

2,3-Dihydro-5-(α-thienyl)-7-trifluoromethyl-1H-1,4-diazepine (IIIa) was obtained from imidazolidine IIa. Yield, 70%, mp 87-88°C (hexane). IR spectrum: 3200 (NH); 1610 (C=N); 1575 (C=C); 1530 cm^{-1} (thiophene ring). PMR spectrum: 3.55 (2H, t, J = 3.0 Hz, CH_2-NH); 4.00 (2H, broad s, CH_2–N=); 5.52 (1H, s, =CH); 7.06 (1H, dd, $J_{H4\text{-}H5}$ = 5.0, $J_{H3\text{-}H4}$ = 3.7 Hz, 4-H_{thioph}); 7.28-7.41 ppm (2H, m, 3-H_{thioph}, 5-H_{thioph}); NH is not observed. Found, %: C 48.51; H 3.80; N 11.27. $C_{10}H_9F_3N_2S$. Calculated, %: C 48.77; H 3.68; N 11.38.

2,3-Dihydro-5-(α-thienyl)-7-(1,1,2,2-tetrafluoroethyl)-1H-1,4-diazepine (IIIb) was obtained from imidazolidine IIb. Yield, 78%, mp 82-83°C (hexane–benzene). IR spectrum: 3200 (NH); 1605 (C=N); 1570 (C=C); 1525 cm^{-1} (thiophene ring). PMR spectrum: 3.52 (2H, t, J = 3.0 Hz, CH_2–NH); 4.00 (2H, broad s, CH_2–N=); 5.60 (1H, s, =CH); 6.25 (1H, tt, $^2J_{H-F}$ = 53.6, $^3J_{H-F}$ = 5.5 Hz, CF_2CF_2H); 7.05 (1H, dd, $J_{H4\text{-}H5}$ = 4.9, $J_{H3\text{-}H4}$ = 3.9 Hz, 4-H_{thioph}); 7.28-7.41 ppm (2H, m, 3-H_{thioph}, 5-H_{thioph}); NH is not observed. Found, %: C 47.46; H 3.49; N 10.03. $C_{11}H_{10}F_4N_2S$. Calculated, %: C 47.48; H 3.62; N 10.07.

2,3-Dihydro-5-phenyl-7-trifluoromethyl-1H-1,4-diazepine (IIIc) was obtained from imidazolidine IIc. Yield, 85%, mp 148-149°C (CCl_4) (literature data [1]: mp 147.5°C). IR spectrum: 3210 (NH); 1615 (C=N); 1580 (C=C); 1530, 1490 cm^{-1} (benzene ring). PMR spectrum: 3.46 (2H, t, J = 3 Hz, CH_2–NH); 3.99 (2H, broad s, CH_2–N=); 5.28 (1H, s, =CH); 4.7-5.6 (1H, broad s, NH); 7.44 ppm (5H, s, C_6H_5). Found, %: C 59.75; H 4.49; N 11.78. $C_{12}H_{11}F_3N_2$. Calculated, %: C 60.00; H 4.62; N 11.66.

2,3-Dihydro-5-phenyl-7-(1,1,2,2-tetrafluoroethyl)-1H-1,4-diazepine (IIId) was obtained from aminoenone Id. Yield, 74%, mp 123-124°C (CCl_4) (literature data [1]: mp 121.5°C). IR spectrum: 3215 (NH); 1605 (C=N); 1575 (C=C); 1530, 1490 cm^{-1} (benzene ring). PMR spectrum: 3.48 (2H, t, J = 3.0 Hz, CH_2–NH); 4.05 (2H, broad s, CH_2–N=); 5.39 (1H, s, =CH); 6.27 (1H, tt, $^2J_{H-F}$ = 53.5, $^3J_{H-F}$ = 5.6 Hz, CF_2CF_2H); 7.3-7.6 ppm (5H, m, C_6H_5); NH is not observed. Found, %: C 57.49; H 4.24; N 10.22. $C_{13}H_{12}F_4N_2$. Calculated, %: C 57.35; H 4.44; N 10.29.

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