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Letters to the Editor

Unusual transformation of a fluoroalkyl-containing β-aminovinyl ketone

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Reactions of β–aminovinyl ketones (AVK) with oxalyl chloride under mild conditions are widely used for the synthesis of substituted 4-acyl-2,3-dihydropyrrole-2,3-diones.[1] Diacylation of fluoroalkyl-containing AVK **1a—c** with oxalyl chloride afforded 5-alkyl-4-polyfluoroacyl-2,3-dihydropyrrole-2,3-diones **2a—c**. Unexpectedly, AVK **1d** proved to give, under analogous conditions, a monoacylation product in the form of chloro lactone **3**. The latter was additionally characterized in the form of methoxy lactone **4**.

Cyclization giving chloro lactones is characteristic of 3-oxocarboxylic acid chlorides.[2] However, no products analogous to compound **3** were obtained earlier by the reactions of oxalyl chloride with AVK-containing compounds.

The synthesis of ketone **1d** was described earlier.[3] The course of the reaction was monitored by TLC on Silufol UV-254 plates in $CHCl_3$. Spot visualization was performed with aqueous solutions of copper acetate and $KMnO_4$ and the iodine vapor. ^1H, ^{19}F, and ^{13}C NMR spectra were recorded on a Bruker DRX-400 spectrometer (400, 376, and 100 MHz, respectively) in $CDCl_3$ with Me_4Si (for ^1H and ^{13}C) and C_6F_6 (for ^{19}F) as the internal standard. IR spectra were recorded on a Perkin Elmer Spectrum One FTIR spectrometer (Nujol). Mass spectra were recorded on a MAT INCOS50 spectrometer (ionizing energy 70 eV, direct inlet probe).

4-(1-Aminoethylidene)-5-chloro-5-(nonafluorobutyl)tetrahydrofuran-2,3-dione (3). Oxalyl chloride (0.62 g, 4.88 mmol) was added to a solution of compound **1d** (1.40 g, 4.62 mmol) in 25 mL of anhydrous chloroform. The reaction mixture was kept at ~20 °C for 48 h and one fifth of the solvent volume was removed *in vacuo*. The precipitate that formed was filtered off and recrystallized from anhydrous chloroform to give compound **3** (1.01 g, 55%), m.p. 157—159 °C (decomp.). Found (%): C, 30.42; H, 1.32; Cl, 8.92; F, 43.65; N, 3.44. $C_{10}H_5ClF_9NO_3$. Calculated (%): C, 30.52; H, 1.28; Cl, 9.02; F, 43.44; N, 3.56. IR, ν/cm^{-1}: 1818, 1644 (C=O), 1590 (C=C), 3232, 3053 (N—H). ^1H NMR, δ: 2.47 (s, 3 H, Me); 6.53 (br.s, 1 H, NH); 11.10 (br.s, 1 H, NH). MS, *m/z* (I_{rel} (%)): 393 $[M]^+$ (4.8), 358 $[M^+ - Cl]^+$ (18.2), 330 $[M - Cl - CO]^+$ (100), 302 $[M - Cl - 2\ CO]^+$ (2), 286 $[M - Cl - 2\ CO - NH_2]^+$(9.3), 219 $[C_4F_9]^+$ (5.7), 146 $[M - C_4F_9 - CO]^+$ (6.7), 138 $[M - C_4F_9 - Cl - H]^+$ (22.4), 83 $[M - C_4F_9 - 2\ CO - Cl]^+$ (11.4), 69 $[CF_3]^+$ (90).

4-(1-Aminoethylidene)-5-methoxy-5-(nonafluorobutyl)tetrahydrofuran-2,3-dione (4). A solution of compound **3** (0.3 g, 0.76 mmol) in 2 mL of anhydrous methanol, which was obtained at 42—45 °C, was kept at ~20 °C for 1 h and cooled. The precipitate that formed was filtered off to give compound **4**

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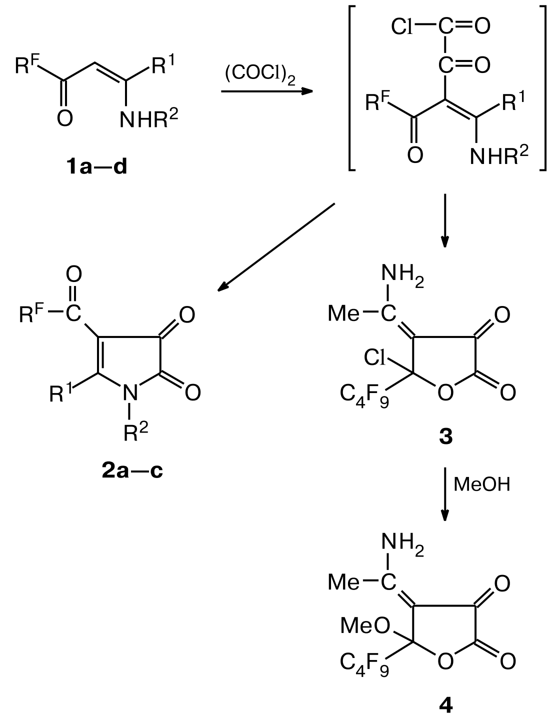
Scheme 1



$R^F = CF_3$ (**a**, **c**); $(CF_2)_4H$ (**b**); C_4F_9 (**d**); $R^1 = Bu^t$ (**a**, **b**); Me (**c**, **d**); R^2 = H (**a**, **b**, **d**); Ph (**c**)

(0.21 g, 70%), m.p. 147—149 °C. Found (%): C, 33.82; H, 2.00; F, 44.58; N, 3.76. $C_{11}H_8F_9NO_4$. Calculated (%): C, 33.95; H, 2.07; F, 43.93; N, 3.59. IR, ν/cm^{-1}: 1804, 1655 (C=O), 3260, 3067 (N—H). ^{1}H NMR, δ: 2.20 (s, 3 H, Me); 3.14 (s, 3 H, OMe); 9.90 (br.s, 1 H, NH); 10.40 (br.s, 1 H, NH). ^{19}F NMR, δ: 36.63—36.97 (m, 2 F, CF_2); 42.08—42.63 (m, 2 F, CF_2); 45.30—45.80 (m, 2 F, CF_2); 82.42 (t, 3 F, CF_3, $^3J_{F,F}$ = 9.8 Hz). MS, *m/z* (I_{rel} (%)): 345 $[M^+ - CO_2]^+$ (1.1), 331 $[M - OCH_3 - CO]^+$ (8.6), 302 $[M - OCH_3 - 2CO]^+$ (27.4), 170 $[M - C_4F_9]^+$ (21.1), 142 $[M - C_4F_9 - CO]^+$ (100), 69 $[CF_3]^+$ (18.9).

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