Polyfluorinated enamines. Synthesis of *N*-(3,3,3-trifluoro-2-trifluoromethylprop-1-enyl)urea

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The considerable interest aroused in recent years in organic compounds containing a trifluoromethyl group is caused, among other reasons, by the potential physiological activity and high lipophilicity of these substances.[1,2] Two pathways to the synthesis of these structures exist. The first method involves modification of starting molecules containing no fluorine with trifluoromethylating or fluorinating reagents. One of the drawbacks of this method, which usually involves a multistep synthesis, is that the yields of the final products are rather low. Therefore, we prefer the second approach, namely, formation of the target structure in one or two steps starting from relatively accessible compounds, incorporating required fragments, synthons. In order to develop a facile method for preparing 5-trifluoromethyluracil possessing high carcinolytic and antiviral activities,[3] we synthesized *N*-(3,3,3-trifluoro-2-trifluoromethylprop-1-enyl)urea (**1**) from urea, H_2SO_4, and *N*-(3,3,3-trifluoro-2-trifluoromethylprop-1-enyl)-dimethylamine (**2**) (the latter was prepared by the reaction of octafluoroisobutene, which is a by-product of the production of fluoroplastics, with DMF[4]):

$$(CF_3)_2C{=}CHNMe_2 \xrightarrow[-Me_2NHSO_4]{H_2NC(O)NH_2,\,H_2SO_4} (CF_3)_2C{=}CHNHC(O)NH_2$$

We have also shown the very real possibility of preparing 5-trifluoromethyluracil in one step, by cyclization and simultaneous partial hydrolysis of compound **1** (at present, this process is being optimized and will be reported later).

Thus, polyfluorinated enamine **2** is a convenient synthetic equivalent of $(CF_3)_2C{=}HC^+$ and probably of $^+C(O)C(CF_3){=}HC^+$.

A 96 % solution of H_2SO_4 (10.2 g, 0.1 mol) was added to a stirred mixture of enamine **2** (20.7 g, 0.1 mol) and urea (6.0 g, 0.1 mol) at such a rate as to maintain the temperature of the reaction mixture below 50 °C. Then 30 mL of cold water was added, and a solution of sodium bicarbonate was added until the pH was 5. The precipitate was filtered off. Recrystallization from water gave 15.1 g of compound **1** (68 %) as colorless needle crystals, m.p. 140 °C (from water), soluble in acetone and ether and sparingly soluble in water. Found (%): C, 27.24; H, 1.89; F, 50.61; N, 12.89. $C_5H_4F_6N_2O$. Calculated (%): C, 27.04; H, 1.82; F, 51.33; N, 12.61. ^1H NMR (acetone-d_6), δ: 6.81 (s, 2 H, NH_2); 7.90 (d, 1 H, CH, $^3J_{H,H}$ = 12.6 Hz); 9.21 (d, 1 H, NH, $^3J_{H,H}$ = 12.6 Hz). ^{19}F NMR (acetone-d_6, CF_3COOH as the external standard), δ: 17.80 (q, 3F, CF_3, $^4J_{F,F}$ = 6.6 Hz); 19.91 (q, 3F, CF_3, $^4J_{F,F}$ = 6.6 Hz). $^{13}C\{H\}$ NMR (CD_3OD), δ: 93.48 (sept, $(CF_3)_2\underline{C}$, $^2J_{C,F}$ = 33.9 Hz,); 122.07 (qd, CF_3, $^1J_{C,F}$ = 271.3 Hz, $^3J_{C,F}$ = 2.7 Hz); 122.52 (qd, CF_3, $^1J_{C,F}$ = 268.6 Hz, $^3J_{C,F}$ = 2.7 Hz); 135.38 (s, CH); 154.04 (s, C=O). MS (EI, 25 eV), *m/z* (I_{rel} (%)): 223 $[M+1]^+$ (14), 222 $[M]^+$ (28), 179 $[M-HNCO]^+$ (100).

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