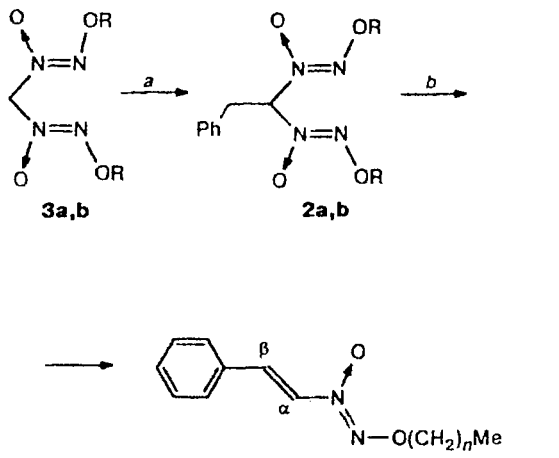

Reagents: *a*. $PhCH_2Cl$, NaOH, Et_4NBr or TEBAC, DMSO; *b*. OH^-.

flash-chromatographed on Silpearl (20 g) using $CHCl_3$ as the eluent. The fraction containing **1a** (2.50 g) was recrystallized from Et_2O to obtain **1a** (1.65 g, 46%) with m.p. 80–81 °C. UV (water), λ/nm (ε): 200 (13700), 232 (8000), 291 (22700). IR (film), ν/cm^{-1}: 3100, 2965, 1480 (N_2O_2), 1310, 1220, 1090, 1050, 995, 885, 865, 850, 780, 710. ^{1}H NMR (*cf.* Ref. 1), δ (10% in DMSO-d_6): 4.12 (s, 3 H, CH_3); 7.42–7.46 (m, 3 H, *m*-H and *p*-H); 7.68 (d, 1 H, α-H, $J_{\alpha,\beta}$ = 13.7 Hz); 7.75–7.78 (m, 2 H, *o*-H); 8.07 (d, 1 H, β-H); (10% in CCl_4): 4.04 (s, 3 H, CH_3); 7.29–7.41 (m, 6 H, H arom. + α-H); 7.60 (d, 1 H, β-H, $J_{\alpha,\beta}$ = 13.3 Hz).

1-(Ethoxy-*NNO*-azoxy)-2-phenylethene (1b) was obtained similarly from **2b**,[2] with benzyltriethylammonium chloride instead of Et_4NBr; R_f for **1b**, 0.12; for **2b**, 0.32; and for **3b**, 0.44. The yield of **1b** was 1.62 g (42%), m.p. 46–47 °C ($CHCl_3$–hexane). ^{1}H NMR (10% in DMSO-d_6), δ: 1.34 (t, 3 H, CH_3, J = 7.1 Hz); 4.40 (q, 2 H, CH_2); 7.40–7.44 (m, 3 H, *m*-H + *p*-H); 7.66 (d, 1 H, α-H, J = 13.5 Hz); 7.73–7.76 (m, 2 H, *o*-H); 8.07 (d, 1 H, β-H). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 192 $[M]^+$ (43), 163 $[M-Et]^+$ (17), 135 (17), 133 $[M-Et-NO]^+$ (89), 117 (16), 116 (10), 106 (12), 105 (19), 104 (47), 103 $[PhCH=CH]^+$ (68), 101 (23), 91 $[PhCH_2]^+$ (20), 90 $[PhCH]^+$ (12), 88 (11), 80 (20), 78 (29), 77 $[Ph]^+$ (100), 63 (14), 51 (45), 49 (22), 39 (12).

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Received December 11, 1997

Polyfluorinated enamines. New methods for the synthesis of 5-trifluoromethyluracil

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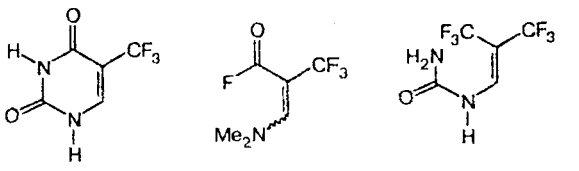
5-Trifluoromethyluracil (**1**) is known to possess high anticancer and antiviral activities.[1] However, the methods for its preparation[2–6] have several disadvantages, such as the multi-stage character,[2] difficultly accessible starting reagents,[3,4] the use of organomercury derivatives,[5] and low yields of the target product.[2,5,6]

We synthesized compound **1** by two new methods, *viz.*, by the reaction of *cis,trans*-3-dimethylamino-2-trifluoromethacryloyl fluoride[7,8] (**2**) with urea and by cyclization with partial hydrolysis of *N*-(3,3,3-trifluoro-2-trifluoromethylprop-1-enyl)urea[9] (**3**). Compounds **2** and **3** were obtained in a few steps from octafluoroisobutene, which is a large-scale by-product of the industrial production of fluoroplastics.



Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 6, pp. 1265–1266, June, 1998.

The reaction of acid fluoride **2** and urea occurs only in the presence of concentrated sulfuric acid.

The transformation of urea **3** into uracil **1** depends on the temperature, pressure, duration of the reaction, compositions of the condensed and gas phases, and the material and design of the reactor. The main side processes (saponification with decarboxylation of trifluoromethyl groups before and after the cyclization of compound **3**) could be prevented by performing the reaction under pressure in a polytetrafluoroethylene vessel in an atmosphere of CO_2.

Reaction of compound 2 with urea and H_2SO_4. Acid fluoride **2** (2.6 g, 0.011 mol) and urea (0.67 g, 0.011 mol) were placed in a quartz flask. 96% H_2SO_4 (1.13 g, 0.011 mol) was added dropwise with ice-water cooling and stirring. Thirty min later, cold water (20 mL) and a solution of $NaHCO_3$ were added to pH 5. The target product was extracted with ether (10×10 mL), and the extract was dried with Na_2SO_4. After evaporation of the ether, compound **1** (1.20 g, 60%) was obtained.

Cyclization of compound 3. A polytetrafluoroethylene tube containing a solution of urea **3** (2.22 g, 0.01 mol) and H_2O (0.18 g, 0.01 mol) in 1,4-dioxane (8 mL) was placed in a steel autoclave with $NaHCO_3$ (5 g). The autoclave was heated at 130 °C for 30 min. The solution was cooled to −20 °C, placed in a quartz flask, and concentrated to half its volume at 13 Torr. Hexane (4 mL) was added. The residue was filtered off and dried to obtain uracil **1** (0.83 g, 46%).

In both cases, the product **1** obtained had m.p. 240–243 °C (decomp.) (*cf.* Ref. 2: 245–246 °C (decomp.)). ^1H NMR (acetone-d_6), δ: 8.10 (m, 1 H, HC); 10.55 (br.s, 1 H, NH); 10.71 (br.s, 1 H, NH). ^{19}F NMR (acetone-d_6, CF_3COOH as the external standard), δ: 14.93 (d, 3 F, CF_3, $^4J_{F,H}$ = 1.08 Hz). The ^{13}C NMR spectrum (DMSO-d_6) corresponds completely to the published data.[10] MS (EI, 70 eV), *m/z* (I_{rel} (%)): 181 $[M+1]^+$ (8), 180 $[M]^+$ (100), 165 $[M-HN]^+$ (3), 161 $[M-F]^+$ (3), 137 $[M-HNCO]^+$ (62), 118 $[M-HNCO-F]^+$ (10), 110 $[M-CF_3-H]^+$ (36), 109 $[M-HNCO-CO]^+$ (15).

This work was financially supported by the Russian Foundation for Basic Research (Project No. 95-03-09332).

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Received December 19, 1997;
in revised form January 26, 1998

Cross-coupling of 4-chloro- and 4-bromocinnolines with alk-1-ynes

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The behavior 4-chloro- and 4-bromocinnoline derivatives, prepared recently by cyclization of *ortho*-ethynylphenyldiazonium salts,[1,2] in the acetylenic condensation has not been studied.

We found that condensation of phenylacetylene with 4-chloro- (**1a**) and 4-bromo-3-phenylcinnoline (**2a**) in the presence of $Pd(PPh_3)_2Cl_2$ and CuI in Et_3N is accompanied by the addition of phenylacetylene to the N=N bond and results in the formation of a compound of a new type, 3-phenyl-1,4-di(phenylethynyl)-1,2-dihydrocinnoline (**3**) instead of the expected 3-phenyl-4-phenylethynylcinnoline (**4a**). In the case of 4-chloro-

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 6, pp. 1266–1267, June, 1998.

1066-5285/98/4706-1233 $20.00