5-POLYFLUOROALKYLURACILS

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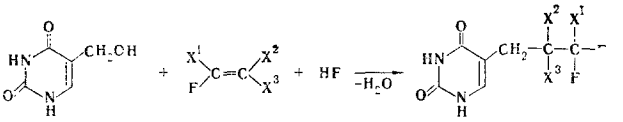
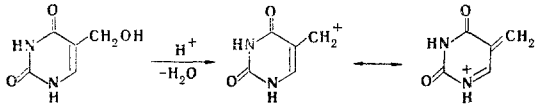
We have accomplished the synthesis of 5-polyfluoroalkyluracils by condensation of 5-hydroxymethyluracil (I) with fluoro olefins in anhydrous HF.



I II

a $X^1=X^2=X^3=H$; b $X^1=F$, $X^2=X^3=H$; c $X^1=X^2=F$, $X^3=H$; d $X^1=X^2=X^3=F$

The reaction occurs via a scheme involving concerted electrophilic addition, in which the driving force is apparently the formation of a stable resonance-stabilized cation from I in acidic media:



EXPERIMENTAL

Dry vinyl fluoride was bubbled through a stirred solution of 6.7 g of I in 100 ml of anhydrous HF at 0° at a rate sufficient to insure complete absorption, after which the HF was evaporated, and the residue was treated with water and neutralized with ammonium bicarbonate to give 3.9 g (44%) of IIa with mp 256-258° (from 50% ethanol). UV spectrum, λ_{max} (50% ethanol), nm (ε): 264 (8100). ^{19}F NMR spectrum (here and subsequently, relative to the CF_3COOH solvent): doublet of triplets (42 ppm), $J_{CHF}=56.4$ Hz, $J_{CFCH}=17.7$ Hz. Found: C 44.3; H 4.5; F 19.4%. $C_7H_8F_2N_2O_2$. Calculated: C 44.2; H 4.2; F 20.0%. The following compounds were similarly obtained: IIb (from I and vinylidene fluoride, 43% yield) with mp 266-269° (from 50% ethanol). UV spectrum, λ_{max} (50% ethanol), nm (ε): 263 (7800). ^{19}F NMR spectrum: triplet (−9.55 ppm), $J_{CFCH}=9.7$ Hz. Found: C 40.5; H 3.5; F 27.0%. $C_7H_7F_3N_2O_2$. Calculated: C 40.4; H 3.4; F 26.4%.

Compound IIc, with mp 261-263° (from 50% ethanol), was obtained in 38.4% yield from I and trifluoroethylene. UV spectrum, λ_{max} (50% ethanol), nm (ε): 261 (7400). ^{19}F NMR spectrum: doublet of doublets (4.29 ppm), $J_{CF_3CF}=11.3$ Hz, $J_{CF_3CH}=6.4$ Hz; multiplet (124.3 ppm), $J_{CHF}=46.7$ Hz (from PMR data). Found: C 37.2; H 2.9; F 33.0%. $C_7H_6F_4N_2O_2$. Calculated: C 37.2; H 2.7; F 33.6%.

A mixture of 7 g of I, 8 g of tetrafluoroethylene and 100 g of HF was stirred at 20° for 4 h in an autoclave. The usual workup gave 2 g of IId with mp 260-262° [purified by adsorption chromatography on silica gel in chloroform-methanol (5:1)]. UV spectrum, λ_{max} (50% ethanol), nm (ε): 262 (7800). ^{19}F NMR spectrum: singlet (9.2 ppm), triplet (41.7 ppm), $J_{CF_2CH_2}=18.5$ Hz. Found: C 34.7; H 2.9%. $C_7H_5F_5N_2O_2$. Calculated: C 34.4; H 2.0%.

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