UNUSUAL REACTIONS OF DIMETHYLPYRIMIDO[4,5-e]- AND [5,4-e]-1,2,4-TRIAZINEDIONES WITH DIETHYLAMINE

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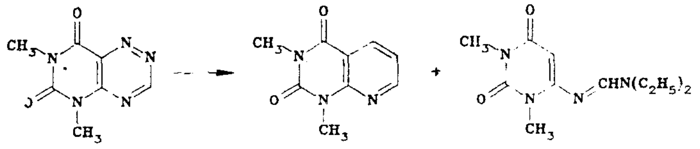
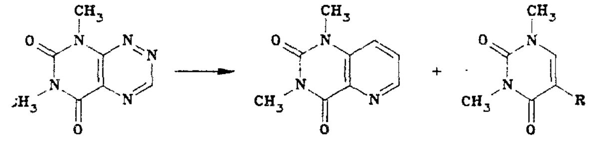
A new method for obtaining pyrido[2,3-d]pyrimidinediones by the (4 + 2) cycloaddition of 5,7-dimethylpyrimido[4,5-e]-1,2,4-triazinedione (I) with enols and enamines was recently discovered [1]. It was found that the product of reverse azadiene synthesis – 1,3-dimethylpyrido[2,3-d]pyrimidinone (II, 65% yield) – is also formed in the reaction of isofervenulin I with diethylamine (with a 270-molar excess of diethylamine, 50°C, 20 h). A second product of this reaction is amidinouracil III, [mp 118-120°C, 34% yield, PMR spectrum ($CDCl_3$): 1.22 and 1.28 (3H each, t, J = 7.2 Hz, $C{-}CH_3$), 3.34 and 3.41 (3H each, s, NCH_3), 3.37 and 3.53 (2H each, q, J = 7.2 Hz, CH_2), 5.05 (1H, s, 5-H), 7.68 ppm (1H, s, N=CH)].


I II III

The natural antibiotic fervenulin (IV) reacts with diethyl-amine under severe conditions (with a 90-molar excess of diethylamine, 150°C, 24 h, in a sealed ampul) to give 1,3-dimethylpyrido[3,2-d]-pyrimidinedione [V, mp 239.5-241.0°C, 11% yield, PMR spectrum (d_6DMSO): 3.35 (3H, s, 3-CH_3), 3.52 (3H, s, 1-CH_3), 7.75 (1H, dd, $J_{7,8}$ = 8.9, $J_{7,6}$ = 4.2 Hz, 7-H), 7.96 (1H, dd, $J_{8,7}$ = 8.9, $J_{8,6}$ = 1.3 Hz, 8-H), 8.55 ppm (1H, dd, $J_{6,7}$ = 4.2, $J_{6,8}$ = 1.3 Hz, 6-H)], amidinouracil VIa [mp91-93°C, 9% yield, PMR spectrum ($CDCl_3$): 1.18 (6H, t, J = 7.2 Hz, $C{-}CH_3$), 3.37 (4H, q, J = 7.2 Hz, CH_2), 3.37 (3H, s, NCH_3), 6.94 (1H, s, N=CH), 8.39 ppm (1H, s, 6-H)], formylaminouracil VIb [mp 203-204°C, 12% yield, PMR spectrum ($CDCl_3$): 3.41 and 3.44 (3H each, s, NCH_3), 7.78 (broad, NH), 8.38 (1H, J = 0.9 Hz, CHO), 8.50 ppm (1H, s, 6-H)], and aminouracil VIc [mp 112-114°C, 3% yield, PMR spectrum ($CDCl_3$): 3.34 and 3.40 (3H each, s, NCH_3), 6.63 ppm (1H, s, 6-H)].


IV V VI a-c

VI a $R{=}NCHN(C_2H_5)_2$; b $R{=}NHCHO$; c $R{=}NH_2$

By special experiments in the case of isoferevenulin I it was established that the source of the 2π component in the cyclo-addition reaction is diethylamine. One of the possible pathways of the formation of the dienophile may be a sequence of reactions that includes one-electron reduction of isofervenulin, generation of the $O_2^{\overline{\cdot}}$ superoxide radical, and oxidation by it of diethyl-amine to vinylethylamine, which then participates in the cycloaddition.

LITERATURE CITED

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