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THE 1,3-DIPOLAR CYCLOADDITION REACTION OF FERVENULIN 4-OXIDES WITH DIMETHYL ACETYLENEDICARBOXYLATE, A NOVEL SYNTHESIS OF PYRROLO[3,2-d]PYRIMIDINES (9-DEAZAPURINES)

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The 1,3-dipolar cycloaddition reaction of fervenulin 4-oxides (6,8-dimethylpyrimido[5,4-e]-as-triazine-5,7(6H,8H)-dione 4-oxides) with dimethyl acetylenedicarboxylate afforded the corresponding 7-carbomethoxy-1,3-dimethylpyrrolo[3,2-d]pyrimidine-2,4(1H,3H)-diones.

The 1,3-dipolar cycloaddition[1] is one of the most useful reactions for the construction of heterocyclic systems and its usefulness is comparable to that of the Diels-Alder reaction in the formation of carbocyclic systems. We now report a novel 1,3-dipolar cycloaddition reaction of fervenulin 4-oxides[2] (6,8-dimethylpyrimido[5,4-e]-as-triazine-5,7(6H,8H)-dione 4-oxides) with dimethyl acetylenedicarboxylate leading to pyrrolo[3,2-d]pyrimidines

(9-deazapurines).

Heating fervenulin 4-oxide (Ia)(0.001 mol) with dimethyl acetylenedicarboxylate (0.0015 mol) in toluene (5 ml) at 95° for 1 hr followed by cooling resulted in the separation of a good yield of 7-carbomethoxy-1,3-dimethylpyrrolo[3,2-*d*]pyrimidine-2,4-(1H,3H)-dione (IIa). Analogous treatment of 3-alkylfervenulin 4-oxides (Ib-c) with dimethyl acetylenedicarboxylate provided the corresponding 6-alkyl-7-carbomethoxy-1,3-dimethylpyrrolo[3,2-*d*]-pyrimidine-2,4(1H,3H)-diones (IIb-c). The structures of (IIa-c) were confirmed by the satisfactory analytical and spectral data. In particular, the unequivocal structure of (IIa) was established by its methylation with dimethylformamide dimethylacetal (95°, 30 min) to 7-carbomethoxy-1,3,5-trimethylpyrrolo[3,2-*d*]pyrimidine-2,4(1H,3H)-dione (IId) which was identical in all respects to the sample prepared from 7-carbomethoxy-3-methylpyrrolo[3,2-*d*]pyrimidine-2,4(1H,3H)-dione (IIe)[3] by the same procedure (Scheme).

Scheme

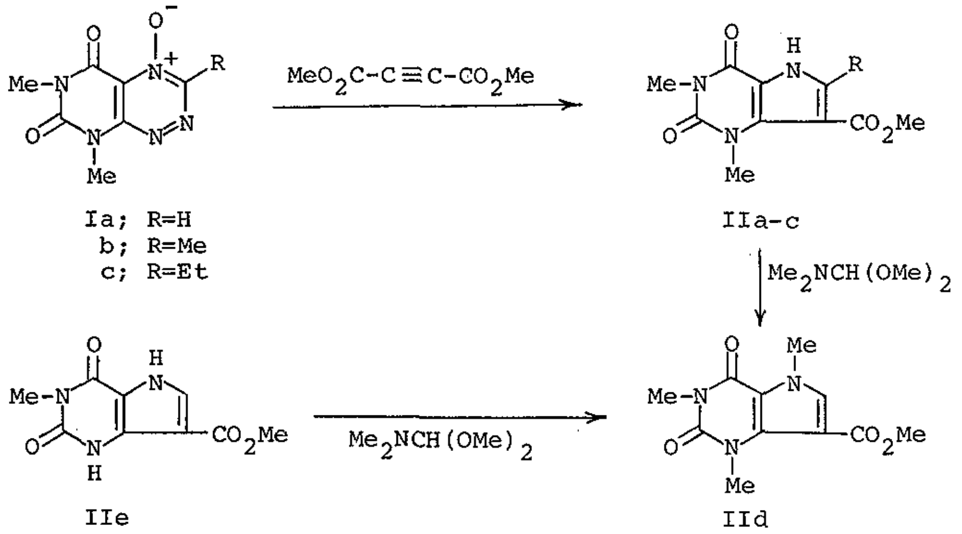

Table Pyrrolo[3,2-d]pyrimidine Derivatives

Compd.[a]	Mp(°C)	Yield(%)	λ max(EtOH)nm(log ε)
IIa	230-231	62	230(4.54) 273(3.91)
IIb	288-289	64	233(4.24) 275(3.73)
IIc	232-233	55	235(4.23) 275(3.60)
IId	201-202	85[b], 53[c]	235(4.23) 273(3.50)

a) All compounds were recrystallized from EtOH. b) From IIa.
c) From IIe.

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