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NEW SYNTHESIS OF PYRIMIDO[5,4-e]-as-TRIAZINES BY THE REACTION OF 6-HYDRAZINO-1,3-DIMETHYL-5-NITROSOURACIL WITH BENZYLIDENETRIPHENYLPHOSPHORANES

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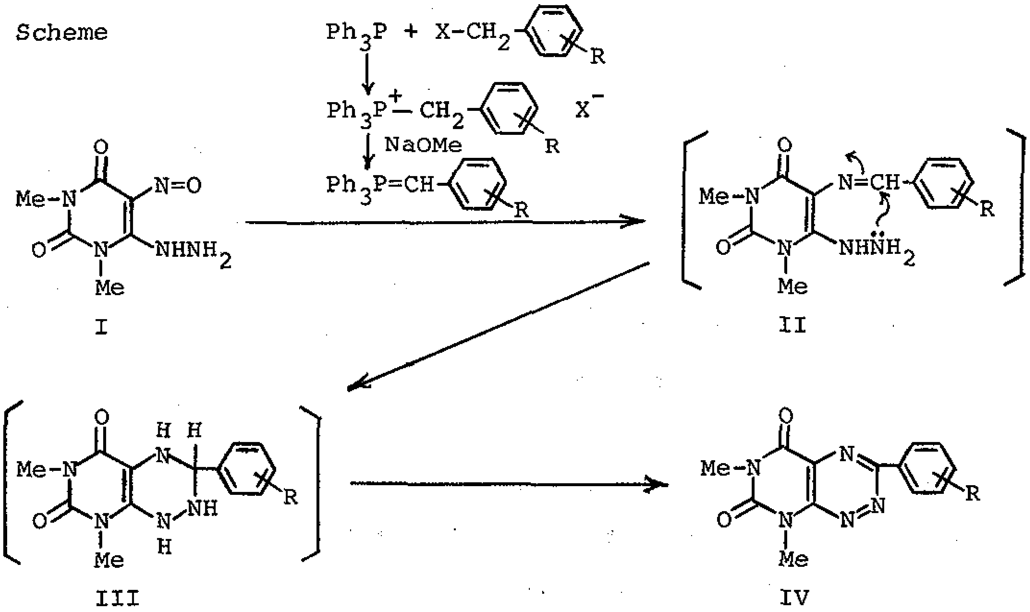
Treatment of 6-hydrazino-1,3-dimethyl-5-nitrosouracil with benzylidenetriphenylphosphoranes gave the corresponding 3-arylfervenulins (3-aryl-6,8-dimethylpyrimido-[5,4-e]-as-triazine-5,7(6H,8H)-diones).

Recent papers[1] from our laboratory described that the reaction of 6-amino-1,3-dimethyl-5-nitrosouracil with benzylidenetriphenylphosphoranes or phenacylidenetriphenylphosphoranes gives purines and pteridines, respectively. In conjunction with these findings and our interest in pyrimido[5,4-e]-as-triazines,[2] we wish to report the reaction of 6-hydrazino-1,3-dimethyl-5-nitrosouracil (I)[3] with benzylidenetriphenylphosphoranes leading to 3-arylfervenulins (3-aryl-6,8-dimethylpyrimido[5,4-e]-as-triazine-5,7(6H,8H)-diones; IVa-e).

Heating of a mixture of I (0.199g, 0.001 mol), sodium methoxide

(0.162g, 0.003 mol), and benzylidenetriphenylphosphonium bromide (prepared by treatment of benzyl bromide (0.256g, 0.0015 mol) and triphenylphosphine (0.393g, 0.0015 mol) in dry dimethylformamide (5 ml) at 90°C for 30 min) at 90°C for 3 hr, followed by evaporation *in vacuo* to dryness, and subsequent dilution with ethanol caused the separation of 3-phenylfervenulin (IVa). Likewise, the reaction of I with other benzylidenetriphenylphosphonium halides afforded the corresponding 3-arylfervenulins (IVb-e) (Table).[4]

Scheme



As depicted in the Scheme, this new pyrimido[5,4-e]-as-triazine synthesis presumably involves the initial formation of the pyrimidine anil (II)[5] by a type of Wittig reaction between the nitroso group of I and benzylidenetriphenylphosphoranes, followed by intramolecular cyclization to (III), and subsequent aromatization. The formation of benzylidenetriphenylphosphoranes seems reasonable, since no reaction was obsereved in the absence of base or triphenylphosphine.

Table 3-Arylfervenulins

Benzyl halide	Product[a]	R	Mp (°C)	Yield (%)
C_6H_5-CH_2Br	IVa	H	273-275	19
4-C_6H_4-CH_2Cl	IVb	4-Cl	280-283	27
3,4-Cl_2-C_6H_3-CH_2Cl	IVc	3,4-Cl_2	259-260	72
4-NO_2-C_6H_4-CH_2Br	IVd	4-NO_2	>300	26
4-Me-C_6H_4-CH_2Cl	IVe	4-Me	286-287	18

a) All products were recrystallized from ethanol.

REFERENCES AND NOTES

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2 a) M. Ichiba, K. Senga, S. Nishigaki, and F. Yoneda, J. Heterocyclic Chem., 1977, **14**, 175; b) K. Senga, M. Ichiba, and S. Nishigaki, Heterocycles, 1977, **6**, 273; c) M. Ichiba, S. Nishigaki, and K. Senga, J. Org. Chem., "accepted"; d) M. Ichiba, S. Nishigaki, and K. Senga, Heterocycles, "accepted."

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4 Compounds IVa-e were identical in all respects with the authentic samples.[2d]

5 The reaction of nitrosobenzene with Wittig reagents has been reported to give the corresponding anils: a) A. Schönberg and K.H. Brosowski, Chem. Ber., 1959, **92**, 2602; b) A.W. Johnson, J. Org. Chem., 1963, **28**, 252.

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