SYNTHESIS OF PYRIMIDINES AND PYRIDO[2,3-d]PYRIMIDINES USING N,S- AND N,N-ACETALS OF DIACETYLKETENE

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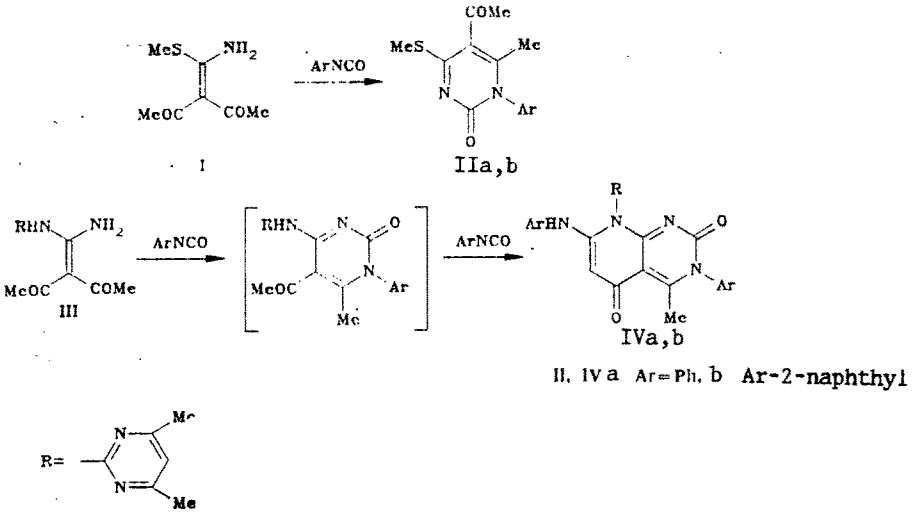
We have recently shown that aminals and N,S-acetals of diacylketones which contain an unsubstituted NH_2 group [1, 2] can be used for the synthesis of a number of heterocyclic systems. It was found that condensation of N,S-acetals of diacetylketene I with arylisocyanates leads to novel pyrimidin-2-ones II. Treatment of the N-(4,6-dimethylpyrimidin-2-yl)aminals of diacetylketene III with ArNCO gives the pyrido[2,3-d]pyrimidin-2,5-diones IV. In this case, the construction of the pyrimidine ring occurs as in the synthesis of II and formation of the pyridine ring via participation of the acetyl CH_3 fragment and a second molecule of the arylisocyanate.



5-Acetyl-6-methyl-4-methylthio-1-phenyl-1H-pyrimidin-2-one (IIa). Compound I [1] (2 mmoles) and PhNCO (2 mmoles) was refluxed in toluene (10 ml) for 2 h. The solvent was evaporated and the residue chromatographed on a silica gel column (40/100) with gradient elution (benzene-1% alcohol in benzene) to give IIa (0.44 g, 80%) with mp 165-166°C (from benzene). PMR spectrum ($CDCl_3$): 1.86 (3H, s, CH_3); 2.55 (3H, s, CH_3); 2.56 (3H, s, CH_3); 7.11-7.53 ppm (5H, m, Ph). $[M]^{+\cdot}$ 274.

5-Acetyl-6-methyl-4-methylthio-1-(2-naphthyl)-1H-pyrimidin-2-one (IIb) was obtained similarly in 74% yield with mp 227-228°C (benzene–hexane, 1:1). $[M]^{+\cdot}$ 324.

8-(4,6-Dimethylpyrimidin-2-yl)-4-methyl-3-phenyl-7-phenylamino-3H,8H-pyrido[2,3-d]pyrimidine-2,5-dione (IVa) was obtained similarly to IIa, b from the ketene aminal III [2] (2 mmoles) and PhNCO (8 mmoles) in 73% yield with mp 325-327°C (from benzene). PMR spectrum ($CDCl_3$): 2.50 (6H, s, $2CH_3$); 2.89 (3H, s, CH_3); 5.52 (1H, s, CH=); 6.80 (1H, s, CH=); 7.11-7.72 (10H, m, 2Ph); 13.66 ppm (1H, s, NH). $[M]^{+\cdot}$ 450.

8-(4,6-Dimethylpyrimidin-2-yl)-4-methyl-3-(2-naphthyl)-7-(2-naphthyl)amino-3H,8H-pyrido[2,3-d]pyrimidine-2,5-dione (IVb) was obtained similarly in 63% yield with mp 341-343°C (from benzene). $[M]^{+\cdot}$ 550.

Elemental analytical data for these compounds agreed with that calculated.

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LITERATURE CITED

1. V. A. Dorokhov and M. F. Gordeev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 4, 941 (1988).
2. V. A. Dorokhov, M. F. Gordeev, Z. K. Dem'yanets, M. N. Bochkareva, and V. S. Bogdanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 8, 1806 (1989).

PHOSPHORYLATED ISOXAZOLES

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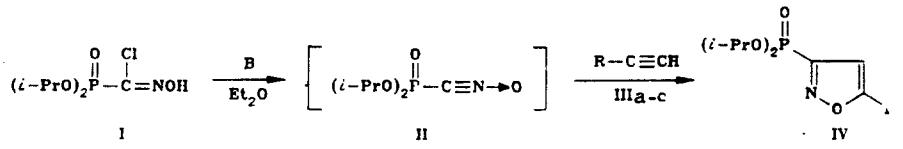
Methods are known for the preparation of phosphorylated heterocycles based on the reaction of ethynylphosphonates with diazo compounds [1, 2] in cycloaddition.

We have shown that diisopropoxyphosphorylchloroformaldoxime (I) in the presence of triethylamine or sodium bicarbonate can serve as a source of diisopropoxyphosphorylnitrile oxide (II), which facilely enters into dipolar cycloaddition with terminal acetylenes (III) at 20°C with formation of previously unknown 3-(diisopropoxyphosphoryl)-5-substituted isoxazoles (IV).



I II IV

B=$NaHCO_3$, NEt_3; IIIa, IV R=C_6H_5; IIIb R=CH_2Br, c R=$COOC_3H_7$-*i*

The process occurs regiospecifically; the yields of isoxazoles IVa-c are 69, 77, and 94%, respectively. The structure of compounds IVa-c was proven on the basis of data of PMR and ^{31}P and ^{13}C NMR spectroscopy. The PMR spectra of all the synthesized compounds in $CDCl_3$ contained a 4-H proton doublet at 6.63-7.20 ppm with spin-spin coupling constant J_{PH} = 0.9-1.5 Hz and also characteristic peaks of the corresponding protons of substituents in the 5 position of the isoxazole ring. The ^{31}P NMR spectra of compounds IVa-c contained the only peak at 2.89, 2.11, and 1.09 ppm, respectively. The data of elemental analysis for all the obtained compounds corresponded to the calculated data.

LITERATURE CITED

1. I. G. Kolokol'tseva, V. N. Chistoketov, B. I. Ionin, and A. A. Petrov, *Zh. Obshch. Khim.*, **38**, 1248 (1968).
2. B. C. Saunders and P. Simpson, *J. Chem. Soc.*, No. 5, 3351 (1963).

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