CONDENSED PYRIMIDOHETEROCYCLIC SYSTEMS

I. The Reaction of 1, 2, 3, 5, 6, 7-Hexahydropyrazolo[1, 5-a]Pyrimidine-5, 7-Dione with Some Amines

L. B. Dashkevich and M. M. Samoletov

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 6, No. 2, pp. 226–227, 1970

UDC 547.854.4'772.2

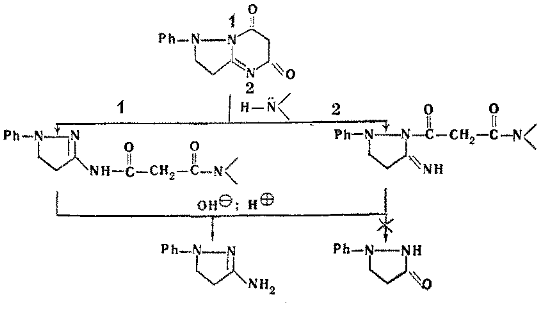
It is shown that reaction of 1, 2, 3, 5, 6, 7-hexahydropyrazolo[1, 5-a]pyrimidine-5, 7-dione with several amines results in the fission of the dioxopyrimidine ring. A mechanism for the ring fission is suggested.

Previous investigations have shown that carbon suboxide undergoes cycladdition reactions with 3-aminopyrazoles to give the corresponding pyrazolo[1, 5-a]pyrimidinediones [1]. It is known from the literature [2] that this type of compound, on heating with aqueous solutions of bases, undergoes disruption of the pyrimidine ring. A similar phenomenon has been observed in the reaction of 1, 2, 3, 5, 6, 7-hexahydropyrazolo[1, 5-a]pyrimidine-5, 7-dione with primary and secondary amines. The amines used in this reaction were piperidine, morpholine, benzylamine, dibutylamine, and di-isobutylamine.

NN'-Hetero Derivatives of Malonyldiamide

Compound	Name	Mp, °C	Molecular formula	Found, %			Calculated, %		
				C	H	N	C	H	N
II	1-Phenyl-3-[N-malonyl(N'-piperidino)]amino-Δ^2-pyrazoline	192—193	$C_{17}H_{22}N_4O_2$	64.73	6.89	17.79	64,96	7.00	17.83
III	1-Phenyl-3-[N-malonyl-(N'-morpholino)] amino-Δ^2-pyrazoline	168—169	$C_{16}H_{20}N_4O_3$	60.58	6.30	17.45	60.76	6.33	17.71
IV	1-Phenyl-3-[N-malonyl(N'-di-isobutylamino)]amino-Δ^2-pyrazoline	162—163	$C_{20}H_{30}N_4O_2$	66.90	8.39	15,86	67,04	8,38	15,64
V	1-Phenyl-3-[N-malonyl(N'-benzylamino)]amino-Δ^2-pyrazoline	148—150	$C_{19}H_{20}N_4O_2$	67.72	6,01	16.72	67.86	5.95	16,66
VI	1-Phenyl-3-[N-malonyl-(N'-dibutylamino)]amino-Δ^2-pyrazoline	135—136	$C_{20}H_{30}N_4O_2$	66,93	8,32	15,75	67,04	8,38	15,64

It is assumed that opening of the pyrimidine ring could occur in two ways:



In order to establish the position of rupture of the pyrimidine ring, the products (see table) were hydrolysed with 15% sodium hydroxide and 17% hydrochloric acid. If fission took place by route 2, then one of the hydrolisis products must be 1-phenylpyrazolidine-3-one. In both cases, however, 3-amino-1-phenyl-Δ^2-pyrazoline was isolated. No depression of the mp was observed on admixture with an authentic sample, and the IR spectra were completely identical in the region from 4000 to 800 cm^{-1}. This proves that the fission occurs by route 1. The structures of the compounds which have been synthesized are put forward on the basis of their elementary analyses and IR spectroscopy.

The presence in the IR spectra of absorption bands at 1690–1680 $\mathrm{cm^{-1}}$ $(-\overset{\overset{\displaystyle O}{\|}}{C}-NH-)$, 1650–1645 $\mathrm{cm^{-1}}$ $(-\overset{\overset{\displaystyle O}{\|}}{C}-N<)$ [3], and also in the valency vibration region at 3343–3340 $\mathrm{cm^{-1}}$ (NH group), confirms the structure of compounds II–VI.

EXPERIMENTAL

Carbon suboxide was prepared by a previously described method [4], and passed directly from the pyrolysis furnace into a benzene solution of 1-phenyl-3-amino-Δ^2-pyrazoline, at the boiling point of the solvent. Compounds II, III, IV, and VI (see table) were prepared by heating the reactants in the starting amine as solvent. Product V was obtained from the reaction of 1 mole of I with 1 mole of benzylamine in dry dioxane; when benzylamine was used as solvent, a product was obtained whose structure has not been determined. When the solid had dissolved, heating was discontinued. Excess of amine was removed in vacuo, ether added to the residue, and the solid was filtered off and washed several times with ether. Ethanol was used as the solvent for crystallization. Compounds II–VI were insoluble in dilute caustic alkalis and mineral acids, but they dissolved in concentrated alkali, mineral acids, methanol, acetone, and dimethylformamide.

REFERENCES

1. L. B. Dashkevich, É. S. Korbelainen, and M. M. Samoletov, KhGS [Chemistry], collection 1, 82, 1967.
2. C. Giunio and P. Giulio, Gazz chim. ital., **65**, 38, 1935.
3. K. Nakanishi, Infra-Red Spectra and the Structure of Organic Compounds [Russian translation], Mir, Moscow, 58, 1965.
4. L. B. Dashkevich, V. A. Buevich, and B. E. Kuvaev, ZhOKh, 30, 1946, 1960.

26 April 1968

Leningrad Chemical and Pharmaceutical Institute