UDC 547.859

CARBON SUBOXIDE AND SOME OF ITS REACTIONS

XXI. Reaction of Carbon Suboxide with Aminopyrimidines*

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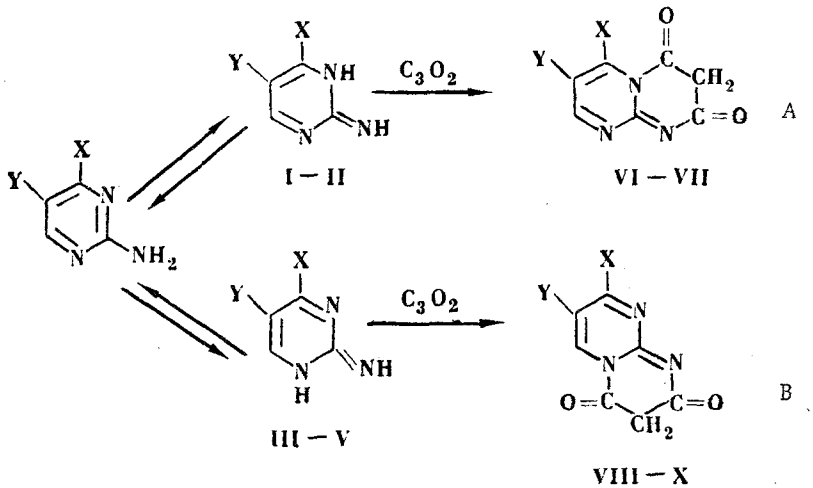
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 1, No. 4, pp. 595-597, 1965

Reaction of carbon suboxide with a number of 2-aminopyrimidines gives compounds which are considered to be 2, 3-(dioxotetrahydropyrimido)pyrimidines or 1, 2-(dioxotetrahydropyrimido)pyrimidines.

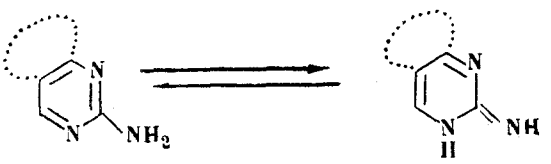
In previous papers the authors showed that a number of heterocyclic amines capable of amine-imine tautomerism react with carbon suboxide to undergo ring closure. The compounds obtained were representatives of hitherto undescribed condensed ring systems, 2, 3-(dioxotetrahydropyrimido)thiazolines [1], 2, 3-(dioxotetrahydropyrimido)benzothiazoles [2], 2, 3-(dioxotetrahydropyrimido)oxazolines (benzoxazolines) [3], etc. In the present work the chemistry of these heterocyclic compounds is described.

Aminopyrimidines can undergo amine-imine tautomerism [5], so that formation of pyrimidopyrimidines by reaction of carbon suboxide with aminopyrimidines could be assumed.

A study has been made of the reaction in the cases of 4-, 5-, and 4, 5-substituted 2-aminopyrimidines, where there were two possible modes of reaction:



while 4, 5(X-V) substituted 2-aminopyrimidines are alicyclo-2-aminopyrimidines:



The literature does not contain any information regarding the manner in which amine-imine tautomerism is affected by substituents in the pyrimidine ring involving the first or third nitrogen atom. Further there are no conclusive chemical or physico-chemical proofs regarding which of the compounds synthesized has formula A, and which formula B. However, it is assumed that the carbon suboxide adds at the most basic ring amine nitrogen (proximity of electron-donor methyl must increase, and phenyl and other electrophilic groups lower, the basicity of the pyrimidine ring nitrogen atom). The structures put forward for the compounds synthesized are assumed, but are the most probable ones.

With carbon suboxide at 50-60° in neutral solvents (ethyl acetate, dioxane, benzene), 2-amino-4-methylpyrimidine (I), 2-amino-4, 5-dimethylpyrimidine (II), 2-amino-4-phenylpyrimidine (III), 2-aminotetrahydroquinazoline (IV), and 2, 3-(2'-aminopyrimido)camphane (V) gave, respectively: 2, 3-(dioxotetrahydropyrimido)-4-methylpyrimidine (VI),

*For Part XX see [4].

2, 3-(dioxotetrahydropyrimido)-4, 5-dimethylpyrimidine (VII), 1, 2-(dioxotetrahydropyrimido)-4-phenylpyrimidine (VIII), 1, 2-(dioxotetrahydropyrimido)tetrahydroquinazoline (IX), 1, 2-(dioxotetrahydropyrimido)-2', 3'-camphanopyrimidine (X).

Using an IKS-12 IR spectrometer with a LiF prism, the spectra of compounds VI-X were measured in the NH group valence vibrations region. The absence of an absorption band in the 3200-3450 cm^{-1} region can be considered to be an indirect proof of the structures proposed (excluding of course the positions of the substituents in the original pyrimidine rings).

Experimental

Preparation of carbon suboxide has previously been described [6, 7]. The starting amines were prepared by known methods. Their mps were those given in the literature [8].

Reaction of carbon suboxide with aminopyrimidines (typical run): A steady stream of carbon suboxide gas was passed through a solution of 0.5 g I in 60 ml benzene. The solution began to turn green, and a greenish precipitate quickly formed. When reaction was complete the precipitate was filtered off. Some further quantity of crystals of VI could be isolated by evaporating the mother liquor.

VII-X were prepared similarly (dioxane being the reaction medium for preparing VII). Compounds VI-X were insoluble in water, ether, slightly soluble in benzene, and quite soluble in ethanol. They were recrystallized from ethanol.

The Table below gives the yields and analytical results for compounds VI-X.

Pyrimidopyrimidines Synthesized

Compound no.	Mp, °C	Formula	Found		Calculated		% yield
			N, %	M	N, %	M	
VI	Decomp. above 310°	$C_8H_7O_2N_3$	23.45 23.52	172	23.72	177	92
VII	268—271*	$C_9H_9O_2N_3$	22.05 22.06	182	21.99	191	94
VIII	309—310	$C_{13}H_9O_2N_3$	17.60 17.67	—	17.57	239	96
IX	228—229	$C_{11}H_{11}O_2N_3$	19.26 19.18	220	17.26	217	90
X	258—259**	$C_{15}H_{17}O_2N_3$	15.72 15.61	260	15.43	271	72

*Raised 10°/min.

**From acetone.

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18 April 1964

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