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TRANSAMINATION OF AZOMETHINES WITH o-ALKYLISOUREAS AS A METHOD FOR THE SYNTHESIS OF 1,2-DIHYDRO-sym-TRIAZINES

N. A. Kapran and V. M. Cherkasov

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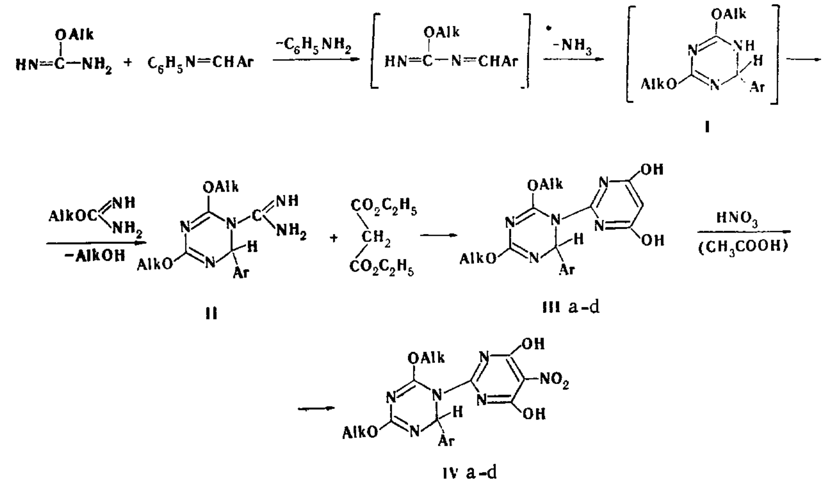
The reaction of o-alkylisoureas with azomethines leads to the formation of 4,6-dialkoxy-2-aryl-1-N-amidino-1,2-dihydro-sym-triazines. 4,6-Dialkoxy-2-phenyl-1-N-(4,6-dihydroxy-2-pyrimidinyl)-1,2-dihydro-sym-triazines were obtained by cyclization of these compounds with malonic ester.

The transamination of azomethines with carboxylic acid amidines, which gives 1,2-dihydro-sym-triazines, was previously studied in [1]. In the present paper we describe the transamination of azomethines with O-alkylisoureas, which can be considered to be analogs of amidines. Instead of the expected dihydro-sym-triazines (I), we obtained 4,6-dialkoxy-2-aryl-1-N-amidino-1,2-dihydro-sym-triazines (II).



II—IV a Alk=CH_3, Ar=C_6H_5; b Alk=CH_3, Ar=p-$(CH_3)_2NC_6H_4$; c Alk=CH_3, Ar=p-$O_2NC_6H_4$; d Alk=C_2H_5, Ar=C_6H_5; e Alk=C_2H_5, Ar=p-$(CH_3)_2NC_6H_4$

The reaction evidently proceeds in the same way with acid amidines, but the resulting dihydro-sym-triazines (I) undergo further reaction as nucleophiles with O-alkylisoureas to give II (Table 1).

Compounds II are colorless crystalline substances that are unstable in air. Like amidines, aqueous solutions of II give a strongly alkaline reaction.

Absorption bands of NH and NH_2 groupings at 3200-3500 and 1550-1590 cm^{-1}, which confirm the presence of an amidine grouping, are observed in the IR spectra of 4,6-dialkoxy-2-aryl-1-N-amidino-1,2-dihydro-sym-triazines II. The same bands are also present in the spectrum of benzamidine.

Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 995-996, July, 1976. Original article submitted July 22, 1975.

TABLE 1. 1-N-Substituted 4,6-Dialkoxy-2-aryl-1,2-dihydro-sym-triazines II-IV

Compound	mp, °C (dec.)	Empirical formula	Found, %			Calculated, %			Yield, %
			C	H	N	C	H	N	
IIa	90—92	$C_{12}H_{15}N_5O_2$	55,4	5,5	26,2	55,2	5,8	26,8	84
IIb	203—204	$C_{14}H_{20}N_6O_2$	55,3	6,9	27,8	55,2	6,6	27,5	68
IIc	229—230	$C_{12}H_{14}N_6O_4$	48,0	3,9	27,6	47,0	4,6	27,4	85
IId	68—70	$C_{14}H_{19}N_5O_2$	59,3	6,4	24,9	58,2	6,6	24,2	38
IIe	166—168	$C_{16}H_{24}N_6O_2$	57,9	7,2	25,8	57,8	7,3	25,3	40
IIIa	218—220	$C_{15}H_{15}N_5O_4 \cdot H_2O$	51,9	4,7	19,7	51,8	4,9	20,2	32
IIId	171—173	$C_{17}H_{19}N_5O_4 \cdot H_2O$	54,9	5,4	20,5	54,4	5,6	19,6	30
IVa	170—172	$C_{15}H_{14}N_6O_6 \cdot H_2O$	45,7	3,8	21,2	45,9	4,1	21,4	60
IVd	191—193	$C_{17}H_{18}N_6O_6$	50,9	4,0	—	50,7	4,7	—	65

The presence of an amidine grouping in II is also confirmed by cyclization with malonic ester to give 4,6-dialkoxy-2-phenyl-1-N-(4,6-dihydroxy-2-pyrimidinyl)-1,2-dihydro-sym-triazines (III). Like 4,6-dihydroxypyrimidine [2], the latter are nitrated by nitric acid to give the corresponding nitro derivatives (IV).

The IR spectra of IV contain the characteristic band of stretching vibrations of nitro groups at 1500 cm^{-1}.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. Monitoring of the course of the reaction and determination of the purity of the products were realized by means of thin-layer chromatography (TLC) on activity II aluminum oxide in a benzene–methanol system (5 : 1) with development by iodine vapors or in UV light.

4,6-Dialkoxy-2-aryl-1-N-amidino-1,2-dihydro-sym-triazines (IIa-e). A solution of 0.02 mole of azomethine and 0.02 mole of O-alkylisourea in 10 ml of dry chloroform was refluxed for 3 h, during which ammonia was evolved. The mixture was cooled, and the precipitated crystals were removed by filtration and washed with chloroform to give a product that was quite soluble in ethanol, acetone, and dioxane.

4,6-Dialkoxy-2-phenyl-1-N-(4,6-dihydroxy-2-pyrimidinyl)-1,2-dihydro-sym-triazines (IIIa, d). A 5.0-mmole sample of 4,6-dialkoxy-2-phenyl-1-N-amidino-1,2-dihydro-sym-triazine (IIa, d) and 5.0 mmole of malonic ester were added to an alcohol solution of sodium ethoxide (from 0.25 g of sodium and 10 ml of absolute ethanol), and the solution was allowed to stand at room temperature for 3 days. The resulting suspension was acidified to pH 3 with 18% HCl, and the precipitate was separated, washed with water, and removed by filtration. The aqueous alcohol filtrate was evaporated, and precipitated III was removed by filtration to give colorless crystals that were only slightly soluble in water and organic solvents.

4,6-Dialkoxy-2-phenyl-1-N-(5-nitro-4,6-dihydroxy-2-pyrimidinyl)-1,2-dihydro-sym-triazines (IVa, d). A 1.0-mmole sample of IIIa, d was added to a mixture of 0.4 ml of fuming nitric acid and 1 ml of glacial acetic acid at 15-20°, and the solution was allowed to stand in an ice bath for 20 min. Ice was then added, and IVa, d gradually precipitated on standing.

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