SYNTHESIS AND THERMAL TRANSFORMATION OF AZOXYPYRIMIDINES

G. G. Moskalenko, V. F. Sedova, and V. P. Mamaev *

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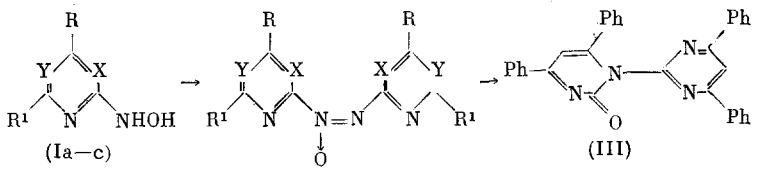
The means of preparation and chemical properties of azoxybenzene derivatives have been studied in sufficient detail [1]. On the other hand, azozypyrimidines have not been described.

We have found that the oxidation of 2- and 4-hydroxyaminopyrimidines† by potassium permanganate in acetone at 20°C gives the corresponding azoxypyrimidines. For example, the oxidation of 2-hydroxyamino-4,6-dimethyl- (Ia), 2-hydroxyamino-4,6-diphenyl- (Ib) and 4-hydroxyamino-6-methyl-2-phenylpyrimidines (Ic) gives 4,4',6,6'-tetramethyl-2,2- (IIa), 4,4',6,6'-tetraphenyl-2,2'- (IIb) and 6,6'-dimethyl-2,2'-diphenyl-4,4'-azoxypyrimidines (IIc) The azoxy products (II) upon heating to their melting point or upon heating in ethylene glycol at reflux rearrange to N-pyrimidinyloxopyrimidines. Thus, azoxy derivatives (IIb) gives 1,2-dihydro-2-oxo-4,6-diphenyl-1-(4,6'-diphenylpyrimidinyl-2')pyrimidine (III). Analogous rearrangements have not been reported for azoxyazines.



(Ia–c) (IIa–c) (III)

X, Y, R, R' = N, CH, Me, Me (a); N, CH, Ph, Ph (b); CH, N, Me, Ph (c).

Product (IIa) was obtained in 58%, mp 138-141°C (dec., from benzene–petroleum ether). Product (IIb) was obtained in 63% yield, mp 184-187°C (dec., reprecipitated from chloroform by the addition of ether). Product was obtained in 65% yield, mp 162–163°C (dec., from ethanol). Product (III) was obtained in 97% yield, mp $> 260°$ (from ethylene glycol).

All the compounds synthesized are stable in the solid state at 20°C. Their structures were confirmed by elemental analysis, IR and PMR spectroscopy and mass spectrometry.

LITERATURE CITED

1. Houben-Weyl, Methoden der Organischen Chemie, Vol. 10/3, G. Thieme Verlag, Stuttgart (1965), p. 467.
2. G. G. Moskalenko, V. F. Sedova, and V. P. Mamaev, Khim. Geterotsikl. Soedin., 1523 (1986).

*Deceased.

†The synthesis of 2- and 4-hydroxyaminopyrimidines has been described in our previous work [2].

All-Union Research Institute for Chemical Means of Plant Protection, Novosibirsk Division. Institute of Organic Chemistry, Siberian Division, Academy of Sciences of the USSR, Novosibirsk. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskya, No. 3, pp. 701-702, March, 1987. Original article submitted November 24, 1986.

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