Rearrangement of 6-Substituted-2,4-Diaminopyrimidines to *s*-Triazines (1)

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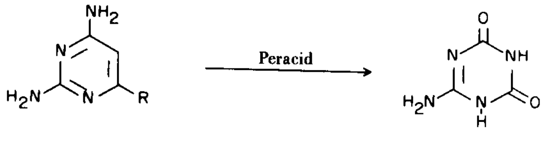
The use of *s*-triazines to prepare heterocyclic compounds including pyrimidines has been noted (2). In fact, the decomposition products of *s*-triazines have been used as the N–C–N fragment in the synthesis of a number of pyrimidine derivatives (3). However, the reverse reaction, the conversion of pyrimidines to *s*-triazines is rather unusual.

In the course of our studies on the peracid oxidation of pyrimidines to the corresponding pyrimidine *N*-oxides (4,5), we encountered a rearrangement of the pyrimidine ring to a *s*-triazine. Treatment of certain 6-substituted-2,4-diaminopyrimidines, **1**, with either peroxyacetic or peroxytrifluoroacetic acids gave compound **2** in good yield. This compound, known as ammelide, has been previously reported (6) and we have confirmed the identity of our products with authentic **2** by spectral and chromatographic comparisons (see Experimental).



1 2

R = Br,Cl,OH,NH$_2$,OC$_6$H$_5$

We are aware of only two other examples of a pyrimidine rearranging to a *s*-triazine. Taylor (7) reports the conversion of 5-nitroso pyrimidines, under Beckman rearrangement conditions, to cyano substituted *s*-triazines. A second example involves the conversion of some 2-alkyl-4-chloro derivatives into *s*-triazines by means of potassium amide in liquid ammonia (8).

The only compounds which lead to the expected *N*-oxide derivatives are the halogenated derivatives. Examination of the groups in position 6 shows that all possess an unshared pair of electrons on the hetero atom and that these groups can contribute to the electron density of the 5,6-double bond. However the halogens being −I groups contribute least, thereby allowing for competitive reactions. Although we have not investigated the possible pathway in any depth it seems clear that electrophilic peracid attack occurs at the susceptible 5 position. This derives support from the fact that such an attack has been observed with ammonium persulfate (9). Furthermore, if the C-5 position is blocked with either a nitro group (5) or a chloro group (10) no such rearrangement takes place.

EXPERIMENTAL (11)

Typical Oxidation Procedure.

The pyrimidine (1.0 g.) was dissolved or suspended in 10 ml. of glacial acetic acid and 90% hydrogen peroxide (1.0 ml.) was added cautiously. The mixture was allowed to stir approximately one day (alternately the mixture could be heated at 50-60° for several hours). The solids were filtered, washed thoroughly with water and dried. Yields ranged between 35-50%. An authentic sample of ammelide was synthesized according to the procedure of Kaiser and Thurston (6b). Infrared data were compared with those of Padgett and Hammer (6a) as well as with the authentic sample obtained. The infrared bands cited below for **2** are composites of the spectra obtained for all our products. The following tabulation of our data is offered to support the identity of **2**:

	Ultraviolet (λ max)			Infrared (cm^{-1})	Paper Chromotography	
	*p*H 1	*p*H 5	*p*H 11		A	B
Ammelide	---	222	226	3350, 1740, 1650 1580, 1470, 1425, 1195, 1000, 782	0.097	0.31
Compound **2**	---	220	226	3340 ± 10, 1740 ± 10, 1650 ± 10, 1580 ± 10, 1470 ± 10, 1420 ± 10, 780 ± 5	0.093	0.30

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(11) Paper chromatography was carried out on Whatman No. 1 paper using the ascending technique. The solvents employed were A; 2-propanol-water-ammonium hydroxide (7:2:1) and B; 1-butanol-acetic acid-water (4:1:1). Ultraviolet spectra were recorded on a Cary 14 spectrophotometer and the infrared spectra were recorded on a Perkin-Elmer 700.

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