

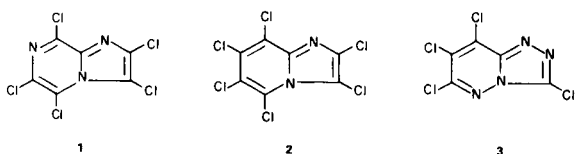
Unusual Fragmentations of Some Polyazaindenes during Perchlorination Reactions

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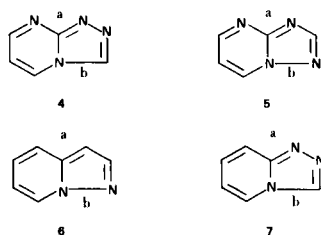
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We have recently described the preparation of perchloroimidazo[1,2-*a*]pyrazine (1) (1), and perchloroimidazo-



[1,2-*a*]pyridine (2) (2). Stanovnick, and Tisler (3), on the other hand, have prepared perchlorotriazolo[4,3-*b*]pyridazine (3).

Our continuing efforts directed, ultimately at the syntheses of perfluoropolyazaindenes prompted us to attempt the preparation of the perchloroderivatives of compounds 4, 5, 6 and 7.

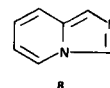


To our surprise, in no instance did we obtain the expected perchloro derivatives, but instead substantial yields of ring-cleaved products were isolated. In each case, cleavage of bonds a and b had occurred to yield perchloropyrimidine from compounds 4 and 5 and perchloropyridine from compounds 6 and 7.

The structures of these products were readily confirmed by comparisons with authentic samples. *A priori*, there

are two differences between these polyazaindenes, and those earlier perchlorinated by us (1 and 2); one is the presence of a N-N bond (4) and the other is that these compounds contain a HC=N-moiety in the 5-membered ring.

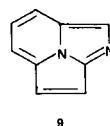
This prompted us to examine the perchlorination of imidazo[1,5-*a*]pyridine (8) which should yield perchloro-



pyridine if the HC=N- bond rather than the -N-N- bond is required for this fragmentation to occur. In fact, when the reaction was done, only perchloropyridine was obtained. Thus, there does not appear to be a need for having 2 nitrogen atoms in the 5-membered ring but rather the presence of a -C=N- structure seems to be indicated.

Another interesting point to mention is that the cyclazine 9, recently described by us (5), does not fragment in the polychlorination reaction, presumably because the -C=N- group is no longer present.

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Unfortunately, we have not yet been able to isolate any intermediates in these reactions and consequently any mechanistic discussions would be premature.

Table

Experimental Details

Starting Material	Reaction Temperature	Product	% Yield	M. p.	M. p. Lit.
4	220°	perchloropyrimidine	52%	62-62°	61-63° (11)
5	220°	perchloropyrimidine	58%	60-62°	61-63° (11)
6	240°	perchloropyridine	48%	123-125°	125-126° (12)
7	230°	perchloropyridine	51%	124-126°	125-126° (12)
8	240°	perchloropyridine	61%	124-126°	125-126° (13)

EXPERIMENTAL

All starting materials were prepared by known procedures.

s-Triazolo[1,5-a]pyrimidine (5).

This compound was prepared in 73.0% yield, m. p. 140-142°, lit. m. p. 140-142° (6).

s-Triazolo[4,3-a]pyrimidine (4).

This compound was prepared in 76.0% yield, m. p. 208-210°, lit. 210-212° (7).

Pyrazolo[1,5-a]pyridine (6).

This compound was prepared in 47.0% yield, b. p. 36-38° at 0.02 torr, lit. b. p. 101° at 22 torr (8).

s-Triazolo[4,3-a]pyridine (7).

This compound was prepared in 63.5% yield, m. p. 36-38°, lit. m. p. 36-38° (9).

Imidazo[1,5-a]pyridine (8).

This compound was prepared by the methods of Fuentes and Paudler, in 81.0% yield, m. p. 55-56°, lit. m. p. 55-56° (10).

Perchlorination Reactions.

General procedure: The appropriate polyazaindene was mixed with a 10 fold molar excess of phosphorus pentachloride and was placed into a stainless steel bomb, which was sealed and heated for 4 hours. The bomb was then cooled and ice was carefully added

to decompose the excess phosphorus pentachloride. The resulting solution was then extracted with chloroform (3 x 100 ml.) and the combined extracts were boiled with charcoal for 10 minutes. The filtered solution was dried (sodium carbonate), refiltered and the filtrate was evaporated *in vacuo* to afford product. The products thus obtained were recrystallized from methanol.

REFERENCES AND NOTES

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