# A Novel Heterocycle Synthesis. Formation of 5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene Dihydroperchlorate by Reaction of Diaminoethane Monohydroperchlorate with Mesityl Oxide or Acetone

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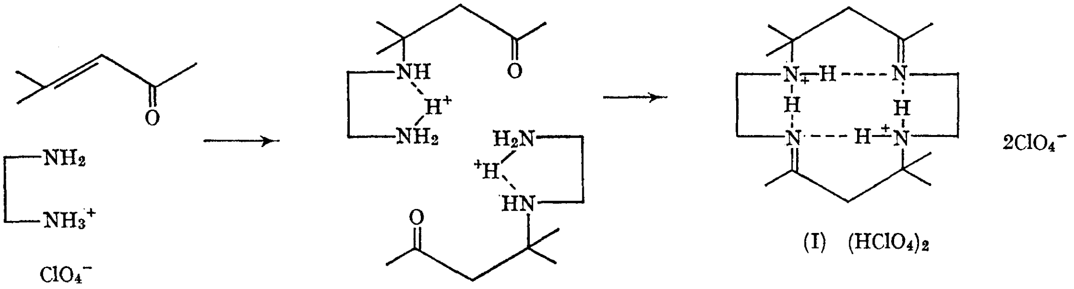
THE formation of the nickel(II) and copper(II) complexes of 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene, (I), by reaction of diaminoethane complexes of the metal ions with acetone has been reported.[1,2] During the course of investigations into the nature of the reactions producing these compounds, it was found that the heterocycle, (I), could readily be prepared in the absence of the metal ions. When the monohydroperchlorate of diaminoethane (prepared by reaction of equimolar amounts of the free diamine and dihydroperchlorate) was dissolved in excess of mesityl oxide, heat was evolved and after a few minutes the dihydroperchlorate of (I) crystallised. (Yield *ca.* 75% based on diaminoethane.) It is suggested that the reaction occurs by the mechanism shown. Firstly a Michael addition of the amine to the $\alpha\beta$-unsaturated ketone produces a substituted $\beta$-amino-ketone.[3] Further reaction with the second amino-group of the diamine is blocked by protonation. (Diaminoethane alone reacts vigorously with mesityl oxide to yield tarry polymeric material, but the dihydroperchlorate shows no reaction.) Pairs of $\beta$-amino-ketone residues then cyclise, by ketimine formation, to yield the heterocycle, (I), which crystallises as the sparingly soluble dihydroperchlorate. The heterocycle was shown to have the configuration (I) by conversion into the nickel(II) complex of known structure, which had been prepared previously by reaction of trisdiaminoethanenickel(II) perchlorate with acetone.[1]



(I) $(HClO_4)_2$

Even more remarkably, a similarly rapid reaction occurs to yield the same product, when diaminoethane monohydroperchlorate is dissolved in acetone. Similar reactions occur with substituted diaminoethanes, and with analogues of mesityl oxide, to yield products analogous to (I), but with different ring substituents on the heterocycle. The scope of the reaction is being studied further.

Endicott and Sadasivan describe a reaction between trisdiaminoethaneiron(II) perchlorate and acetone which yields a mixture of the dihydroperchlorate of (I) and an oxide of iron.[4] They also report the preparations of some metal ion complexes of (I) from the dihydroperchlorate.[4] We consider that the iron(II) perchlorate in their reaction is serving the same function as the perchloric acid in the reaction reported in this Communication, *i.e.*, the blocking of the polymerisation reaction, followed by generation of perchloric acid to give the insoluble dihydroperchlorate of (I).

The formation of the heterocycle, (I), in the absence of metal ions raises questions concerning the role of the metal ion when the nickel(II) and copper(II) complexes of diaminoethane react with acetone. A similar pathway could be followed, the metal ion serving as a blocking agent to polymerisation, then possibly as a template for the cyclisation and finally stabilising the heterocycle as the metal-ion complex. However, the fact that the complexed diamines react with acetone, but not with mesityl oxide indicates that there are differences.

Moreover, when trisdiaminoethanenickel(II) reacts with acetone, complexes of two isomeric heterocycles are formed, one with the secondary amine groups *trans* and another with these groups *cis* (*i.e.*, with one of the mesityl oxide residues reversed). Thus, for the formation of the *cis*-complex at least, the nickel(II) ion is sterically controlling the reaction.

(*Received, July* 1*st*, 1966; *Com.* 453.)

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[1] N. F. Curtis, Y. M. Curtis, and H. J. K. Powell, *J. Chem. Soc.* (*A*), 1966, in the press.

[2] N. F. Curtis, *J. Chem. Soc.*, 1960, 410; M. M. Blight and N. F. Curtis, *ibid.*, 1962, 3016.

[3] M. E. Smith and H. Adkins, *J. Amer. Chem. Soc.*, 1938, **60**, 407.

[4] J. F. Endicott and N. Sadasivan, private communication, to be published.