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HETEROCYCLIC SYNTHESIS BY MEANS OF MERCURIC SALTS. II(1)

SYNTHESIS OF BICYCLIC SYSTEMS

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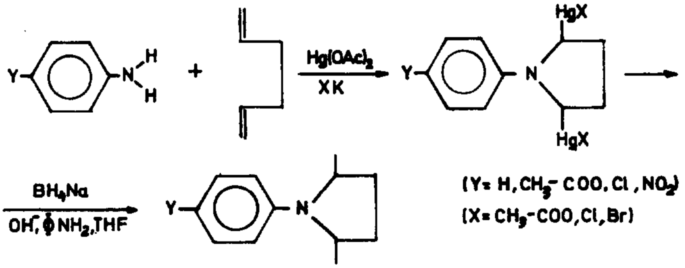
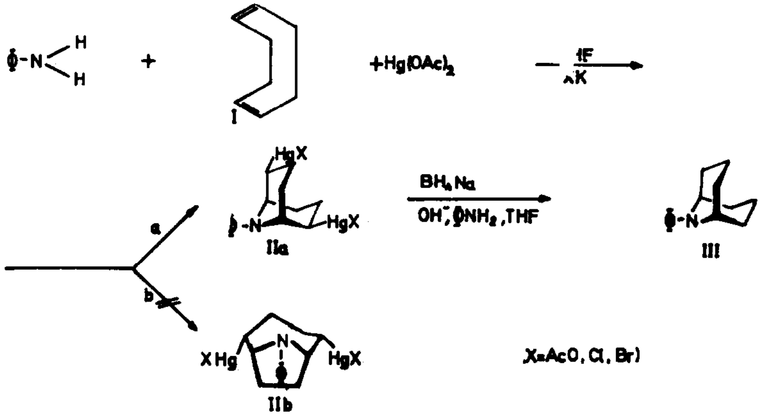
Secondary aliphatic amines bind to olefinic double bonds in the presence of mercuric ; in an aminomercuration reaction(2-9). This reaction occurs in a similar fashion to the known oximercuration of olefins in the presence of water, alcohols and acids, although eaction is much more laboured (it needs a long reaction time) due to the strong Hg-N action (3,10).

In a previous paper(1) we described the addition of primary aromatic amines to an chain diene system, 1,5-hexadiene which, by means of an intermolecular heterocyclization ion, leads to mercurated pyrrolidine systems, which when further reduced give the sponding derivatives of pyrrolidine.

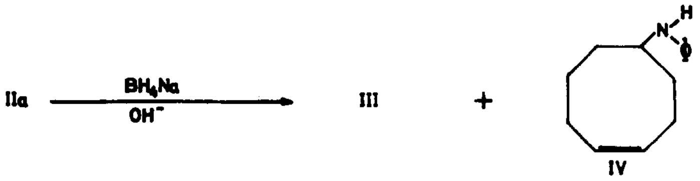


This reaction is similarly produced with a cyclic diene, cis-cis-1,5-cyclooctadiene. ercuration with mercuric acetate and aniline in THF gives only the aza-bicyclic mercuric unds IIa which on subsequent reduction gives N-Phenyl-9-aza-bicyclo [3,3,1] nonane III.



The reduction with $NaBH_4$ is very easy and occurs in the direction indicated in 1N Na aniline and THF as the reaction media. However when Brown's (11) method is employed a secondary amine IV appears with a double bond in the chain, as well as the compound III. T compound IV comes from a desaminomercuration reaction. The proportions of compounds III a IV change with the alkalinity of the medium. (*).

Rearrangement reactions have not been observed in any case.



Both the aminomercuration reaction and the reduction are complete in less than a hour at room temperature, with an overall yield of III higher than 80 %.

The elementary analyses, molecular weight, and also IR, NMR and double resonance spectra, agree in all cases with the structures indicated.

In order to draw generalisations from these reactions of aminomercuration with intermolecular heterocyclization we are at an advanced stage in the study of the synthesi of cyclic and bicyclic systems with two or more equal or different heteroatoms in the rin We are also studying the mechanism of reduction with $NaBH_4$ in order to determine the fact leading to demercuration and desaminomercuration respectively.

(*): The reaction of desaminomercuration has been found in the reduction of an other ser of aminomercuric compounds (12).

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