

## Mercury(II) Oxide–Tetrafluoroboric Acid-promoted 1,4-Cycloamination of 1,3-Dienes. Synthesis of 9-Azabicyclo[4.2.1]non-7-enes and 3-Pyrrolines

José Barluenga,\* Julia Pérez-Prieto, and Gregorio Asensio

*Departamento de Química Orgánica, Facultad de Química, Universidad de Oviedo, Oviedo, Spain*

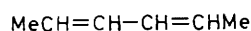
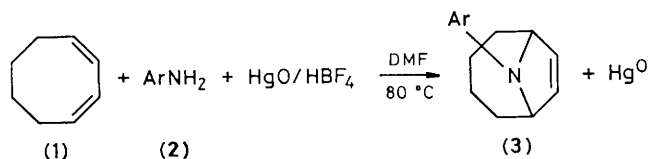
A new and simple method for the direct one-step 1,4-cycloamination of conjugated dienes is described.

The solvomercuration–demercuration of alkenes is a widely used synthetic procedure which provides a very convenient route for the Markownikoff addition of nucleophiles to mono-olefins and non-conjugated dienes.<sup>1</sup> By contrast, little is known about the mercuration of 1,3-dienes except for the hydration reaction.<sup>1,2</sup> On the other hand, buta-1,3-diene is diaminomercured by a mixture of mercury(II) acetate and aniline *via* attack of mercury at the two terminal positions of the diene system and addition of two molecules of amine to the adjacent positions.<sup>3</sup>

We have now found that linear and cyclic 1,3-dienes react with primary aromatic amines and mercury(II) oxide–tetra-

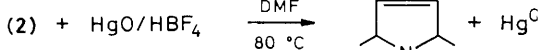
fluoroboric acid<sup>4</sup> to afford 1,4-cycloamination products in good yields in a ‘one pot, one step’ process.† Reactions were carried out in *N,N*-dimethylformamide (DMF) solution at 80 °C for 4 h and a twofold excess of 1,3-diene was employed. Elemental mercury precipitated quantitatively in the course of the reaction. Reaction products (3) and (5) were purified

† 1,4-Diamination of 1,3-dienes by palladium complexes has been recently described: J.-E. Backvall and J.-E. Nystrom, *J. Chem. Soc., Chem. Commun.*, 1981, 59; B. Akermark, J. E. Backvall, A. Lowenborg, and K. Zetterberg, *J. Organomet. Chem.*, 1979, **166**, C33.

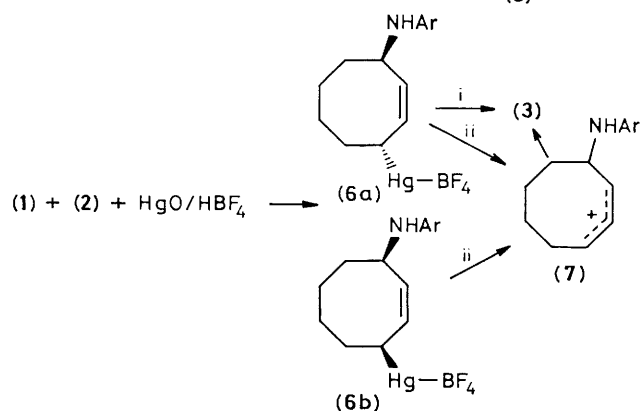


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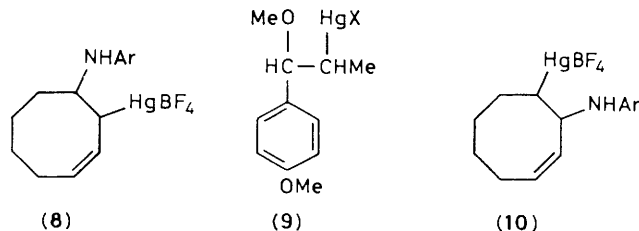
(5)



Scheme 1

by column chromatography (silica; toluene-hexane-diethylamine 75:15:10) and were characterized by elemental analyses and i.r., <sup>1</sup>H n.m.r., and <sup>13</sup>C n.m.r. spectroscopy (including off-resonance experiments).

We have already shown that β-aminomercury(II) tetrafluoroborates are polar enough to undergo nucleophilic attack by the lone electron pair of an amine,<sup>4</sup> ether,<sup>5</sup> or alcohol<sup>6</sup> at the C-Hg bond. On these grounds, the 1,4-cycloamination of 1,3-dienes could be envisaged as proceeding through the formation of an intermediate 1,4-adduct (6) in which mercury is displaced by amine with direct participation of the nucleophile in an assisted breakage of the *anti* C-Hg bond (6a; path i) or by spontaneous reduction of mercury in the intermediate allylic organomercurial (6a or 6b; path



ii).<sup>‡</sup> Since cycloaminations occur not only with cyclic, but also with linear, dienes the (*Z*)-configuration around the double bond should be fixed in the intermediate 1,4-adduct as a result of the stereochemistry of the aminomercuriation step, at least if reactions follow path i (see Scheme 1).

Another possibility is the formation of an intermediate 1,2-adduct (8) from which (7) could be generated. However, this latter alternative is ruled out if we consider the directive effect of both conjugated double bonds and aryl groups on the oxymercuration. For instance, cyclohexa-1,3-diene is mono-oxymercured-demercured to afford cyclohex-2-en-1-ol.<sup>2b</sup> We have found, by <sup>13</sup>C n.m.r. analysis of the crude reaction product, that methoxymercuration of *p*-MeOC<sub>6</sub>H<sub>4</sub>-CH=CHMe is regiospecific and leads to the formation of (9); *i.e.*, attack by mercury seems to occur at the terminal positions of conjugate π-systems. This occurs not only when these positions consist of =CH<sub>2</sub> groups (*e.g.* Markownikoff addition to buta-1,3-diene or penta-1,3-diene)<sup>2b</sup> but also when the diene framework is composed exclusively of =CH-units. As a consequence, the 1,2-aminomercuriation of (1) would be expected to yield the regioisomer (10) instead of (8) and, hence, this route would not afford cycloamination compounds (3) and (5) and is disregarded.

Because of the simplicity and availability of all reagents used, our new 'one pot, one step' method for the 1,4-cycloamination of 1,3-dienes described above should be of wide applicability in the synthesis of simple and bicyclic Δ<sup>3</sup>-unsaturated five membered nitrogen-containing heterocycles.

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Table 1. 1,4-Cycloamination of conjugated dienes.

Diene	Amine (Ar)	Compound	Yield, %
(1)	Ph	(3a)	45
(1)	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	(3b)	62
(1)	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	(3c)	56
(1)	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub>	(3d)	53
(1)	<i>m</i> -MeC <sub>6</sub> H <sub>4</sub>	(3e)	43
(4)	Ph	(5a)	58
(4)	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	(5b)	44

<sup>‡</sup> The reductive intramolecular displacement of mercury is a general process in reactions with β-amino- and β-alkoxy-substituted organomercuric tetrafluoroborates: see refs. 4–6.