

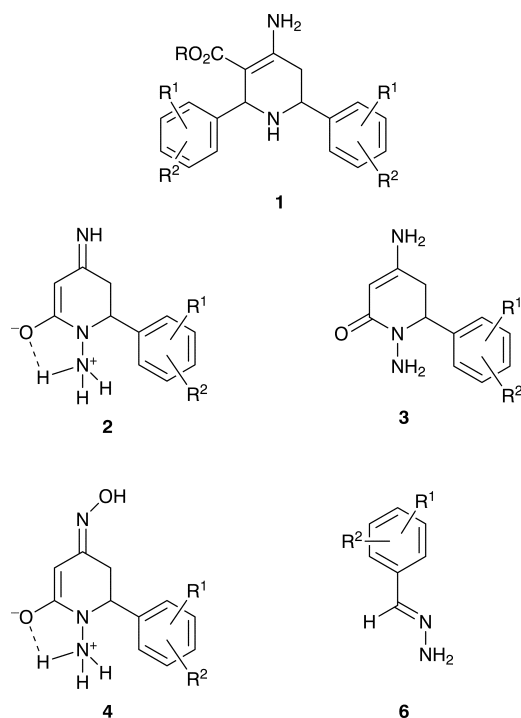
# Conversion by Hydrazinolysis of Tetrahydropyridine Ester Derivatives into 1-Ammoniotetrahydropyridine 6-oxide Derivatives

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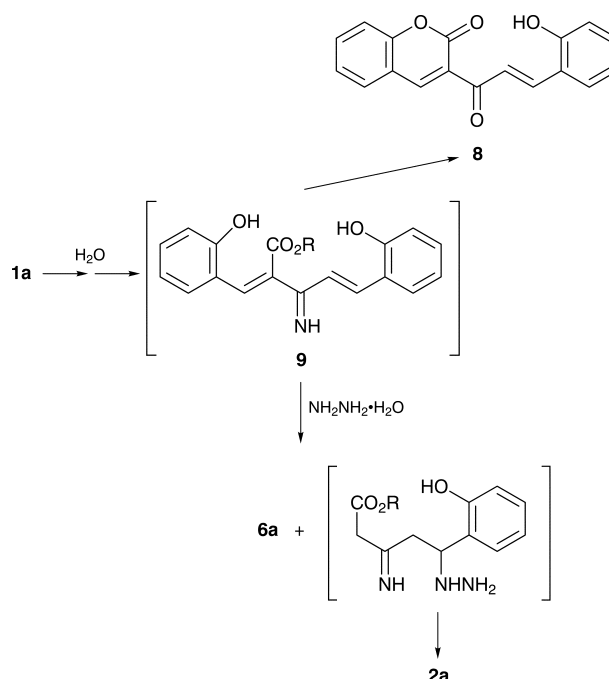
The reaction of alkyl 4-amino-2,6-diaryl-1,2,3,6-tetrahydropyridine-5-carboxylates with hydrazine hydrate results in the formation of 1-ammonio-2-aryl-4-imino-1,2,3,4-tetrahydropyridine 6-oxides, with elimination of one aryl group and the ester alkoxy group.

Ring transformations of heterocyclic structures, which involve hydrazinolytic ring-opening followed by ring closure, are comparatively rare.<sup>1</sup> The reaction now reported consists of the hydrazinolytic conversion of alkyl 4-amino-2,6-diaryl-1,2,3,6-tetrahydropyridine-5-carboxylates **1** into 1-ammonio-2-aryl-4-imino-1,2,3,4-tetrahydropyridine 6-oxides **2**.



**a** R = Me, R<sup>1</sup> = 2-OH, R<sup>2</sup> = H  
**b** R = Me, R<sup>1</sup> = 4-OMe, R<sup>2</sup> = H

The parent compounds in this reaction are substituted derivatives of the tetrahydropyridine esters **1**; when the 2-hydroxyphenyl derivative **1a** is heated with an excess of hydrazine hydrate in ethanol under reflux, hydrazinolysis occurs with elimination of one of the aryl groups and the ester methoxy group. The products are identified as the 2-hydroxybenzylidene hydrazone **6a** and a mono-aryl pyridine derivative formulated as the ionic structure **2a**. The predominance of a zwitterionic structure **2a** (rather than a pyridinone structure *e.g.* **3a**) is indicated by the IR spectrum which features strong salt bands in the 3150–2500 cm<sup>-1</sup> region, with only an extremely weak carbonyl band at 1634 cm<sup>-1</sup>. A strong, non-salt absorption band at 3384 cm<sup>-1</sup> is attributed to the imino group; the presence of the latter is confirmed by the ease with which an oxime **4a** is formed. The *p*-methoxy derivative **2b**, which is similarly obtained from the reaction of the ester **1b**<sup>2</sup> with hydrazine hydrate,



Scheme

has a very similar IR spectrum to that of **2a**. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of these products are in accord with the formulation **2**.

An indication of the mechanism involved is provided by the fact that, when the diaryl ester **1a** is heated in water, hydrolysis affords the benzopyran derivative **8**. It seems probable that this reaction involves an intermediate of type **9**; if a similar intermediate is formed in the presence of hydrazine hydrate, hydrazinolytic cleavage would liberate the 2-hydroxybenzylidene fragment as a hydrazone **6a** (*cf.* ref. 4). The residual ester would then afford the product **2a** by addition of hydrazine and cyclic hydrazone formulation (see Scheme).

Techniques used: IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR

References: 11

Schemes: 1

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