

## Novel Synthesis and Rearrangement of 6-Azabicyclo[3.1.0]hex-3-en-2-ones

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Reaction of *N*-aminopyridinium iodides with cyclopentadienone derivatives gave the 6-azabicyclo[3.1.0]hex-3-en-2-ones (**3**) which rearranged to the hydroxypyridine derivatives (**4**) upon heating or irradiation.

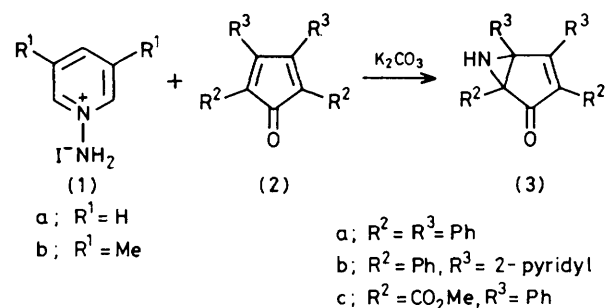
We have previously reported the novel reaction of *N*-aminopyridinium salts with 2,5-dimethyl-3,4-diphenylcyclopentadienone giving new tricyclic pyridinium ylides.<sup>1</sup> During subsequent investigations on the reaction of *N*-aminopyridinium salts with cyclopentadienones possessing more bulky substituents, we have found another interesting reaction to give 6-azabicyclo[3.1.0]hex-3-en-2-one derivatives.

When an acetonitrile solution of 1-aminopyridinium iodide (1.2 equiv.) (**1a**) and tetraphenylcyclopentadienone (**2a**) was heated at reflux in the presence of potassium carbonate for 4 h, compound (**3a**) was obtained in 27% yield as pale yellow crystals, m.p. 170–171 °C, as the only isolable product. Compound (**3a**) was also obtained in 20% yield in the reaction of (**1b**) with (**2a**). The structure of (**3a**) was determined on the basis of spectroscopic data along with chemical evidence. Elemental analyses and its mass spectrum indicate that (**3a**) is a product formed by elimination of pyridine from a 1 : 1 adduct of the pyridinium *N*-imide and the cyclopentadienone. Its

i.r. spectrum shows NH [ $\nu_{\text{max}}$  (KBr) 3420 cm<sup>-1</sup>] and conjugated CO peaks (1704 cm<sup>-1</sup>), and a <sup>1</sup>H n.m.r. resonance at  $\delta$  3.31 due to NH. Heating (**3a**) in refluxing xylene gave the hydroxypyridine derivative (**4a**) (m.p. 206–207 °C, 60%), confirming the aziridine structure. This reaction giving the 6-azabicyclo[3.1.0]hexenone system is a new type of a reaction for aziridine formation and analogous to that of pyridinium phenacylides with cyclopentadienones giving bicyclo[3.1.0]hex-3-en-2-ones.<sup>2</sup> The formation of (**3a**) can be explained by nucleophilic attack of the pyridinium *N*-imide on (**2a**) to give the intermediate (**5**) followed by pyridine elimination.

In contrast, the reaction of the dimethyl compound (**1b**) with the di-(2-pyridyl)cyclopentadienone (**2b**) under the same conditions as those for (**2a**) afforded the aziridine (**3b**) (m.p. 172–173 °C, 11%) and the hydroxypyridine (**4b**) (m.p. 238–240 °C, 3%). The aziridine (**3b**) rearranged to (**4b**) quantitatively when heated in refluxing xylene. In the reaction of (**1a**) and (**1b**) with the bismethoxycarbonyl substituted cyclopenta-

dienone (2c), only the hydroxypyridine derivative (4c) (m.p. 232–234 °C) was obtained in 45 and 38% yields, respectively.

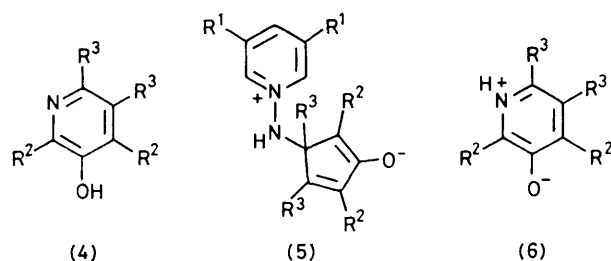


This contrasting reactivity of the various cyclopentadienones (2) can be attributed to the difference in the thermal stability of the resulting aziridines (3). The products (3a) and (3b) are the first examples of *N*-unsubstituted 6-azabicyclo[3.1.0]hex-3-en-2-ones to be reported although there are a few reports on the preparation of *N*-substituted derivatives.<sup>3,4</sup> In recent years valence isomerization between 6-azabicyclo[3.1.0]hex-3-en-2-ones and pyridinium-3-olates has attracted considerable attention.<sup>3,5</sup> The thermal rearrangement of (3) to (4) can be rationalized by a mechanism involving the pyridinium-3-olate (6) as an intermediate. Irradiation of a benzene solution of (3a) and (3b) with a 400 W high-pressure mercury lamp afforded the hydroxypyridine (4a) and (4b) in 89 and 88% yields, respectively.

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## References

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Scheme 1