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

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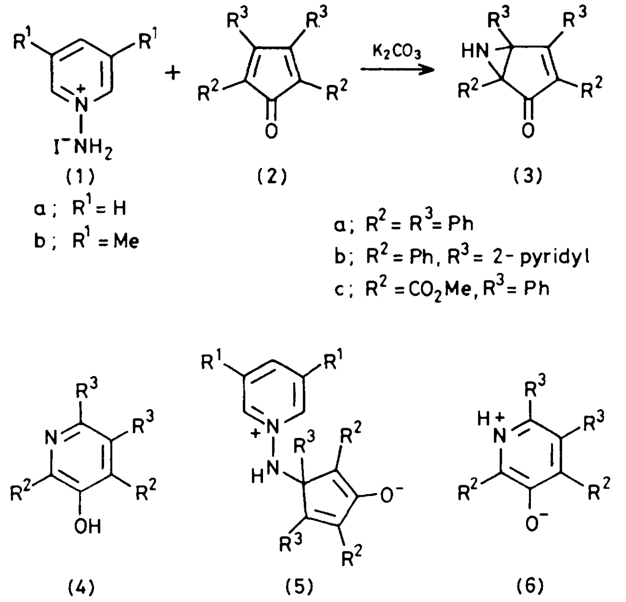
Reaction of *N*-aminopyridinium iodides with cyclopentadienone derivatives gave the 6-azabicyclo[3.1.0]hex-3-en-2-ones (**3**) which rearranged to the hydroxypyridine derivatives (**4**) upon heating or irradiation.

We have previously reported the novel reaction of *N*-aminopyridinium salts with 2,5-dimethyl-3,4-diphenylcyclopentadienone giving new tricyclic pyridinium ylides.[1] 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 [ν_{max} (KBr) 3420 cm^{-1}] and conjugated CO peaks (1704 cm^{-1}), and a ^{1}H n.m.r. resonance at δ 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.[2] 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 cyclopentadienone (**2c**), only the hydroxypyridine derivative (**4c**) (m.p. 232—234 °C) was obtained in 45 and 38% yields, respectively.



Scheme 1

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.[3,4] In recent years valence isomerization between 6-azabicyclo[3.1.0]hex-3-en-2-ones and pyridinium-3-olates has attracted considerable attention.[3,5] 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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