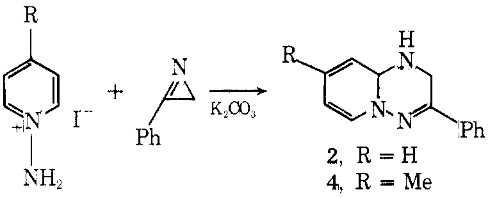
Reaction of Pyridinium *N*-Imines with 2-Phenylazirine

Summary: Pyridinium *N*-imine hydriodides **1** and **3** reacted with 2-phenylazirine in the presence of alkali to give the corresponding 3-phenyl-1,9a-dihydro-2*H*-pyrido[1,2-*b*]-*as*-triazine derivatives **2** and **4** in good yields.

Sir: In the course of studies on the chemistry of pyridinium ylides, we recently reported the first synthesis of pyridotriazine derivatives from the reaction of pyridinium *N*-imines with α-haloacrylates. Mechanistic considerations suggested that the corresponding aziridine or azirine derivative as intermediate might be involved in this reaction.[1] This possibility has now confirmed by isolation of the 3-phenylpyridotriazines **2** and **4** from the reaction of pyridinium *N*-imines with the readily available 2-phenylazirine.

When the mixture of pyridinium *N*-imine hydriodide **1** with 2-phenylazirine[2] was treated with potassium carbonate in methylene chloride at room temperature for 4 days, a new compound **2** (mp 95–97°) was formed in 73% yield. *Anal.* Calcd for $C_{13}H_{13}N_3$: C, 73.90; H, 6.20; N, 19.89. Found: C, 73.93; H, 6.22; N, 19.73. Similar treatment of 4-methylpyridinium *N*-imine hydriodide **3** with the azirine afforded the corresponding compound **4** (mp 112–115°) as yellow crystals in 65% yield. *Anal.* Calcd for $C_{14}H_{15}N_3$: C, 74.64; H, 6.71; N, 18.65. Found: C, 74.57; H, 6.69; N, 18.62. (See Scheme I.)

Scheme I



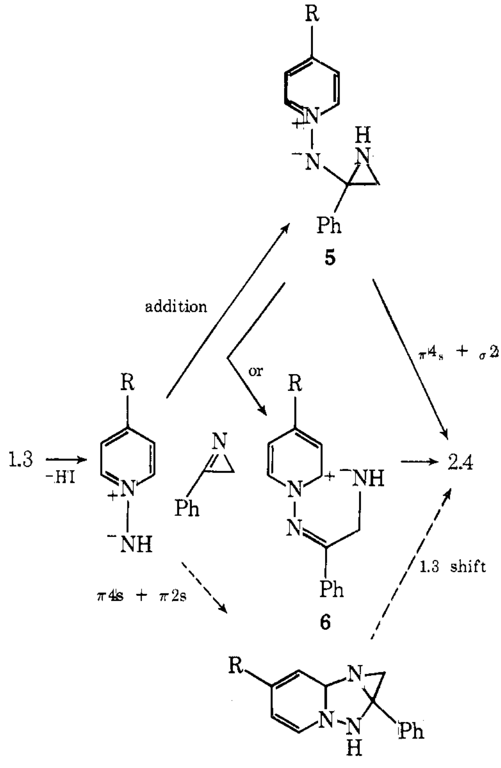
1, R = H
3, R = Me

2, R = H
4, R = Me

Compounds **2** and **4** were 1:1 adducts of the corresponding *N*-imines and 2-phenylazirine, and the ir spectra showed characteristic absorption for a secondary amino group at 3225 (**2**) or 3240 cm^{-1} (**4**) and a carbon–nitrogen or carbon–carbon double bond at 1637 (**2**) or 1654 cm^{-1} (**4**), respectively. The ^1H nmr spectrum of compound **2** exhibited signals due to five protons of the dihydropyridine ring at δ ($CDCl_3$) 4.74 (1 H, br t, J = 7.5, 7.5, 1.5 Hz, C_7 H), 5.23 (1 H, br d, J = 11.0 Hz, C_9 H), 5.42 (1 H, br s, C_{9a} H), 5.99 (1 H, m, C_8 H), and 6.62 (1 H, d, J = 7.5 Hz, C_6 H), an amino proton at δ 2.00 (1 H, br s), two methylene protons at δ 3.74 (1 H, d, J = 18.0 Hz) and 4.07 (1 H, d, J = 18.0 Hz), and five aromatic protons in the range of δ 7.1–7.5. The ^1H nmr spectrum of **4**, compared with that of **2**, showed the absence of one proton signal in the olefinic region and the presence of a new methyl signal at δ 1.79 (3 H, d, J = 1.5 Hz). These assignments were also supported by the correspondence of the ring proton signals in the spectra of **2** and **4** and of 2-methyl-3-methoxycarbonyl-1,9a-dihydro-2*H*-pyrido[1,2-*b*]-*as*-triazine, prepared earlier by us.[1] From these results, we conclude that compounds **2** and **4** are 3-phenyl-1,9a-dihydro-2*H*-pyrido[1,2-*b*]-*as*-triazine and its 8-methyl homolog.

The reaction probably proceeds *via* initial electrophilic addition of 2*H*-azirine to the *N*-imines, followed by homo-1,5-dipolar cyclization ($_{\pi}4_s$ + $_{\sigma}2_s$) of resulting *N*-(2-aziridinium)iminopyridinium ylide **5** or by cyclization of 1,6-dipolar species **6** from **5** to give pyridotriazines **2** and **4** (path a). Similar addition reactions to azirine are well known.[3] An alternative route (path b) to **2** and **4** involves initial 1,3-dipolar cycloaddition ($_{\pi}4_s$ + $_{\pi}2_s$) of the *N*-imines with the azirine followed by 1,3 shift of the amino hydrogen in the primary tricyclic adduct **7**. Since such thermal 1,3 shift is a symmetry-forbidden process,[4] the 1,3 migration should be proceed *via* not sigmatropic but ionic process under such basic condition as employed here.[5] The possible reaction mechanisms are shown in Scheme II.

Scheme II



7

⟶ path a
--→ path b

In this reaction path a seems to be more probable than path b, because 1,3-dipolar cycloaddition of 2-phenylazirine with various N-substituted iminopyridinium ylides was unsuccessful. Further investigation of this reaction is in progress.

References and Notes

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