Rearrangement of 2-Ethynylpyridinium *N*-Imides to Pyrazolo[2,3-*a*]pyridines

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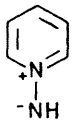
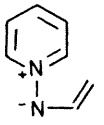
Summary Pyrazolo[2,3-*a*]pyridines (**6**) are obtained from the *N*-amino-2-ethynylpyridinium salts (**5**) on treatment with base.

THE 1,3-dipolar cycloaddition[1] of the pyridinium *N*-imides (**1**) to olefins or acetylenes and the intramolecular 1,5-dipolar cyclisation[2] of the vinylazomethine imides (**2**) have been widely investigated. However, few such reactions of pyridinium *N*-imides with an unsaturated substituent in the 2-position of the pyridine ring are known. Therefore we were interested in examining the thermal behaviour of 2-ethynylpyridinium *N*-imides in connection with studies on the thermal rearrangements of the propynylammonium ylides (**3**)[3–5] and now report our results.



(1)



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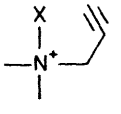
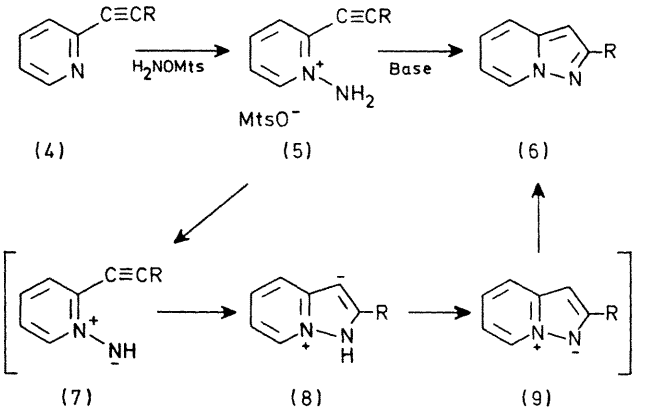


(3) a, X = O
b, X = N
c, X = CH

The ethynylpyridines (**4**) were aminated with *O*-mesitylsulphonylhydroxylamine[6] to give the salts (**5**) in 70—90% yields, which were then treated with potassium carbonate in dimethylformamide at room temperature to yield the corresponding pyrazolo[2,3-*a*]pyridines (**6**)† as the sole products.

A possible mechanism for the reaction is shown in Scheme 1, although none of the intermediates could be isolated. The propynylammonium *N*-oxides (**3a**)[4] and *N*-imides (**3b**)[5] are



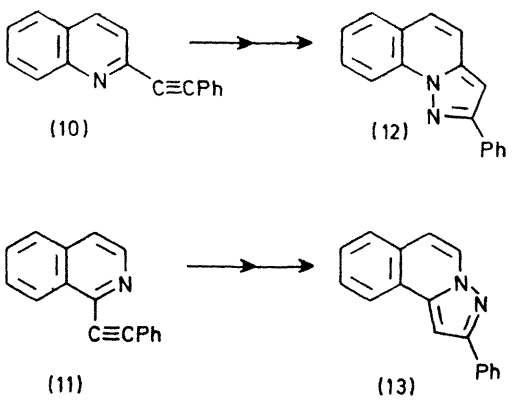
(4) (5) (6) (7) (8) (9)

Mts = mesitylsulphonyl

SCHEME 1. **a**; R = H
b; R = Ph
c; R = CH_2OH
d; R = Bu^n

† The new compounds (**6c**: oil; 75%) and (**6d**: oil; 85—90%) were characterized by elemental analysis and by spectral comparison with compounds (**6a**: oil; 15—20%) and (**6b**: m.p. 106—107 °C; 95%) already reported (ref. 7).

known to undergo a thermal [2,3] sigmatropic rearrangement to generate allene derivatives. However, a concerted mechanism for the present reaction seems unlikely because of prohibitive ring strain in the corresponding five-membered cyclic allene intermediate.



SCHEME 2

Similarly, the pyrazoloquinoline (**12**: m.p. 86—87 °C; 20—25%) and pyrazoloisoquinoline (**13**: m.p. 115–116 °C; *ca.* 10%) were also obtained, from 2-ethynylquinoline (**10**) and 1-ethynylisoquinoline (**11**) derivatives, respectively.

Pyrazolo[2,3-*a*]pyridines with an electron withdrawing substituent such as an acyl, cyano or nitro group in the 1- and/or 2-position can be prepared from the pyridinium *N*-imides (**1**) or (**2**) by 1,3-dipolar cycloaddition to acetylenes or 1,5-dipolar cyclisation, but unsubstituted and alkyl-substituted pyrazolo[2,3-*a*]pyridines are little known.[7] The present result provides a useful new method for preparing simple pyrazolo[2,3-*a*]pyridines.

Part of this work was supported by a Grant-in-Aid for Special Project Research from the Ministry of Education, Science and Culture, Japan.

(*Received*, 8*th July* 1980; *Com.* 745.)

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