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ISOMERIZATION IN THE ALKYLATION OF *cis*-STYRYLPYRIDINE

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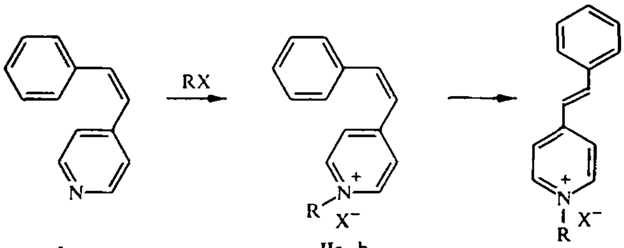
There have been many studies on various aspects of the *cis–trans* thermal and photochemical isomerization of azastilbenes and their quaternary salts [1-3], although several questions have not yet been fully elucidated. Thus, the *cis*-1-methyl-2-(2-phenylethenyl)pyridinium salt was found to form in alkylation of *cis*-2-styrylpyridine by methyl tosylate [2].



I IIa, b IIIa, b

II, III a R = CH$_3$, b R = CH$_2$Ph: X = Cl, I, OSO$_2$Ph

In the present work, we discovered that only *trans*-styrylpyridinium derivatives are isolated quantitatively upon reaction of *cis*-4-styrylpyridine (I) with alkylating agents.

In order to determine the possibility of forming *cis*-1-alkyl-4-styrylpyridinium (II), PMR spectroscopy was used to study the products of the reaction of stilbazole I with methyl iodide, methyl benzoylsulfonate, and benzyl chloride as alkylating agents. For this purpose, the reaction was carried out at 40°C in methanol-D$_4$ in an NMR tube with constant monitoring of the reaction mixture. We found that *cis*-pyridinium isomers II are formed as intermediates and rapidly convert to *cis*-pyridinium isomers III. The maximum content of IIa in the mixture was 25% in the case of methyl iodide. In all cases, only *trans*-isomer III is found in the reaction mixture upon 100% conversion of starting stilbazole I.

A sample of *cis*-styrylpyridine I was prepared in 45% yield by the Wittig reaction using isonicotinaldehyde and benzyltriphenylphosphonium bromide, bp 105°C (0.5 mm Hg), n_D^{25} = 1.6216. PMR spectrum: 6.42 (1H, d, J = 12.03 Hz, $-$CH=), 6.74 (1H, d, J = 12.03 Hz, CH=), 7.06 (2H, d, β-H Py), 7.20 (5H, m, Ph), 8.40 ppm (2H, d, α-H Py).

Only spectral evidence was obtained for the formation of *cis*-styrylpyridinium IIa. PMR spectrum in methanol-D$_4$ (δ, ppm, data given for nonoverlapping signals): 3.34 (3H, s, CH$_3$), 6.54 (1H, d, J = 12.3 Hz, $-$CH=), 6.76 (1H, d, J = 12.3 Hz, $-$CH=). The formation of *cis*-styrylpyridinium IIb (maximum content about 10%) was observed only relative to the vinyl proton signals in the PMR spectrum: 6.56 (1H, d, J = 12.3 Hz, $-$CH=), 6.79 ppm (1H, d, J = 12.3 Hz, CH=).

Samples of *trans*-styrylpyridinium iodide (IIIa) isolated from the reaction mixture and obtained by the methylation of *trans*-4-styrylpyridine had identical physicochemical indices, mp 215°C. PMR spectrum: 4.30 (3H, s, CH$_3$), 7.36 (3H, m, Ph), 7.45 (1H, d, J = 16.14 Hz, CH=), 7.67 (2H, m, Ph), 7.92 (1H, d, J = 16.14 Hz, CH=), 8.16 (2H, d, β-H Py), 8.82 (2H, d, α-H Py).

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REFERENCES

1. L. Horwitz, J. Org. Chem., **21**, 1039 (1956).
2. J. L. R. Williams, S. K. Webster, and J. A. van Allan, J. Org. Chem., **26**, 4893 (1961).
3. K. Tahagi, H. Usami, H. Fukaya, and Y. Sawahi, J. Chem. Soc., Chem. Commun., No. 16, 1174 (1989).