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SYNTHESIS AND CHARACTERIZATION OF 1-IMIDOYLIMINOPYRIDINIUM N-YLIDES

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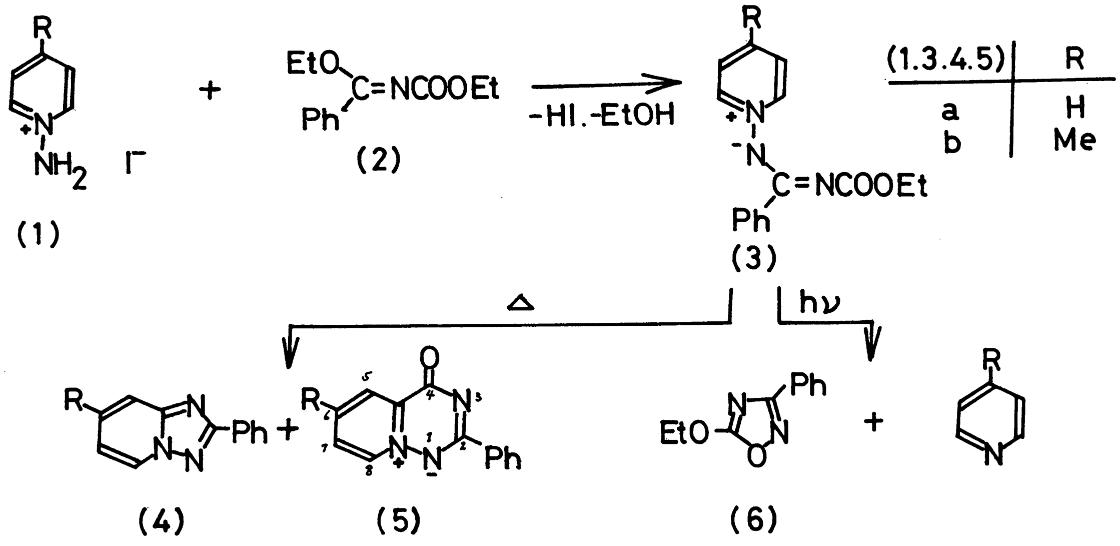
1-Imidoyliminopyridinium N-ylides were prepared for the first time by the reaction of pyridinium N-imines with ethyl benzimidate, and their thermal and photochemical reactivities were examined.

Pyridinium N-ylide is a remarkable species as a 1,3- or 1,5-dipole and its synthetic utility for various nitrogen-bridged heterocycles has been well documented in recent years.$^{1)}$ As a part of our investigation on pyridinium N-ylide, we now wish to report the first synthesis and characterization of 1-imidoyliminopyridinium N-ylides.

As in preparations of other substituted 1-iminopyridinium N-ylides,$^{1)}$ the reactions of 1-aminopyridinium iodides(1a,b) with ethyl N-ethoxycarbonylbenzimidate(2) in ethanol in the presence of potassium carbonate gave the title compounds, 1-imidoyliminopyridinium N-ylides(3a; mp 132-133°C, ν^{KBr} 1655 cm^{-1}, λ_{max}^{EtOH} 251(logε 4.22) and 338 nm(logε 3.37), and 3b; mp 128-130°C, ν^{KBr} 1663 cm^{-1}, λ_{max}^{EtOH} 249(logε 4.24) and 330 nm(logε 3.40)) as colorless needles in 74 and 88% yields, respectively.$^{2)}$ These N-ylides(3a,b) are very stable under ordinary conditions, but they were thermolyzed in refluxing xylene to give two types of compounds(4a; 36%, colorless needles, mp 135-137°C and 5a; 58%, yellow needles, mp 232-234°C, ν^{KBr} 1603 and 1404 cm^{-1}, λ_{max}^{EtOH} 253(logε 4.43) and 343 nm(logε 4.15), δ($CDCl_3$) 7.50(3H, m, m, m′ and p-protons of phenyl), 7.88(1H, bt, J=8.0, 7.0, 2.0 Hz, 7-H), 8.13(1H, bt, J=8.0, 7.5, 1.0 Hz, 6-H), 8.42(2H, m, o and o′-protons of phenyl), 8.72(1H, dd, J=7.5, 2.0 Hz, 5-H) and 8.82(1H, dd, J=7.0, 1.0 Hz, 8-H), and 4b; 38%, colorless needles, mp 140-142°C and 5b; 51%, yellow needles, mp 245°C(dec), ν^{KBr} 1610 and 1388 cm^{-1}, λ_{max}^{EtOH} 252(logε 4.43) and 344 nm(logε 4.21), δ($CDCl_3$) 2.63(3H, s, 6-CH_3), 7.50(3H, m, m, m′ and p-protons of phenyl), 7.65(1H, dd, J=7.0, 2.5 Hz, 7-H), 8.50(3H, m, o and o′-protons of phenyl and 5-H) and 8.70(1H, d, J=7.0 Hz, 8-H)). On the other hand, photolysis of N-ylide(3a) in acetone using high-pressure mercury lamp afforded a colorless crystalline product(6; mp 31-33°C) in 64% yield together with considerable



amounts of pyridine(detected by tlc). The same compound(6) was also obtained by irradiation of N-ylide(3b) in 60% yield. These results are shown above.

Compounds(4a and 6) were assigned to be 2-phenyl[1,2,4]triazolo[5,1-a]pyridine and 5-ethoxy-3-phenyl-1,2,4-oxadiazole by comparisons with authentic samples,3) and N-ylides (3a,b) were determined by their physical and spectral inspections and by comparison with other pyridinium N-ylides. The formation of compounds(3a,b, 4a,b and 6) can be also realized by the mechanistic speculation. Compounds(5a,b) were concluded to be triazanaphthalene derivatives with six-membered mesoionic structure, since signals attributable to protons on the pyridine ring in the NMR spectra appear only in aromatic region, and spectral patterns in the UV spectra are similar to those of parent N-ylides(3a,b). In particular, the enhanced extinction coefficients in compounds(5a,b) suggest clearly the increase of coplanarity for transition in ylidic structure. These IR and NMR spectra are also grossly similar to those of mesoionic diazanaphthalene.4) Further details and scope of these reactions will be reported in near future.

REFERENCES AND NOTES

1) A. Kakehi and S. Ito, J. Org. Chem., 39, 1542(1974), and references cited therein.
2) Satisfactory elemental analyses were obtained for all new compounds reported here.
3) a) T. Okamoto, M. Hirobe, Y. Tamai, and E. Yabe, Chem. Pharm. Bull., 14, 506(1966).
b) J. D. Bower and G. R. Ramage, J. Chem. Soc., 4506(1957).
4) Recently we obtained similar mesoionic diazanaphthalene in photolysis of 1-vinyliminopyridinium N-ylide. See A. Kakehi, S. Ito, T. Funahashi, and Y. Ota, J. Org. Chem., in press.

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