

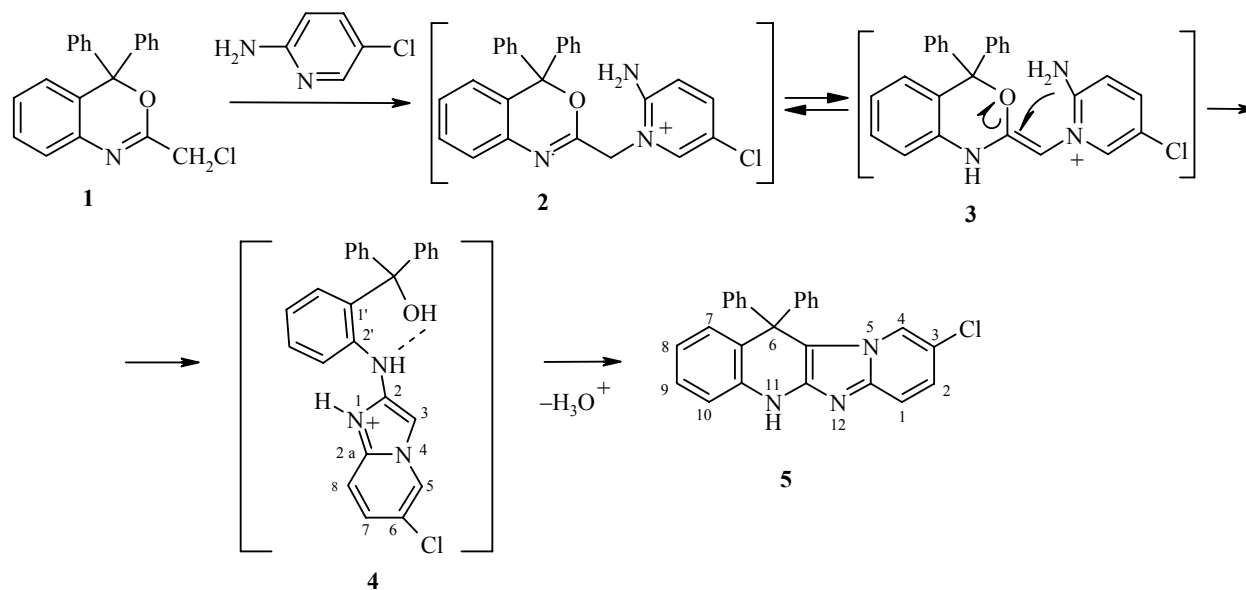
SYNTHESIS OF 3-CHLORO-6,6-DIPHENYL-6,11-DIHYDROPYRIDO[1',2':1,2]IMIDAZO[4,5-*b*]QUINOLINE BASED ON REACTION OF 2-CHLOROMETHYL-4,4-DIPHENYL-4H-3,1-BENZOXAZINE WITH 2-AMINO-5-CHLOROPYRIDINE

E. V. Gromachevskaya and G. D. Krapivin

Keywords: 4H-3,1-benzoxazines, 6,11-dihydropyrido[1',2':1,2]imidazo[4,5-*b*]quinoline, alkylation, mass spectral decomposition.

In an extension of research on synthesis and study of the properties of substituted 4H-3,1-benzoxazines [1], we have carried out reactions of 2-chloromethyl-4,4-diphenyl-4H-3,1-benzoxazine (**1**) with a number of nucleophiles.

We found that reaction of benzoxazine **1** with 2-amino-5-chloropyridine (boiling the starting materials in absolute alcohol in the presence of K_2CO_3 [2]) occurs in an unusual manner and leads to formation of a novel heterocyclic system. We have established that both nitrogen atoms of the reagent enter into the reaction. We hypothesize that alkylation of the pyridine nitrogen atom occurs first. After this, a 1,3-prototropic shift occurs in the initial alkylation product **2**, leading to intermediate **3**, and then opening of the oxazine ring at the $C_{(2)}-O$

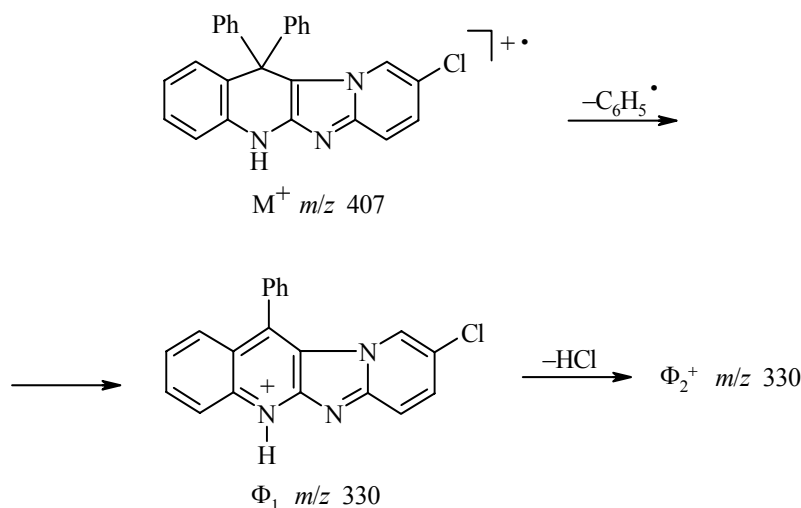


Kuban State University of Technology, Krasnodar 350072, Russia; e-mail: organics@kubstu.ru. Soedinenii, No. 10, pp. 1586-1588, October, 2004. Original article submitted December 20, 2003.

bond leads to formation of an imidazo[1,2-*a*]pyridine system **4**. Then as a result of intramolecular electrophilic substitution of the proton at C₍₃₎ of the imidazole ring, closure of the dihydropyridine ring occurs and the tetracyclic structure **5** is formed.

3-Chloro-6,6-diphenyl-6,11-dihydropyrido[1',2':1,2]imidazo[4,5-*b*]quinoline (5). Yield 50%; mp >235°C (alcohol). IR spectrum (vaseline oil), ν , cm⁻¹: 3300 (NH), 1580 (C=C), 1540 (C=N). ¹H NMR spectrum (Bruker WM-350, SF = 250 MHz, DMSO), δ , ppm (*J*, Hz): 6.75 (1H, m, H-10); 6.90 (1H, d, *J*₁₋₂ = 5.0, H-1); 7.25 (15H, m, 13H_{arom}+H₂+H₄); 9.60 (1H, s, NH). Mass spectrum (Varian CH-6), *m/z* (*I*_{rel}, %)*: 407 (10); 332 (35); 330 (100); 294 (13); 203 (3); 163 (7); 147 (3); 135 (6); 91 (3); 83 (5); 78 (6). Found, %: C 76.35; H 4.85; Cl 10.55; N 8.42; *m/z* 407 [M]⁺*. C₂₆H₁₈ClN₃. Calculated, %: C 76.56; H 4.42; Cl 10.31; N 8.71.

Initial decomposition of compound **5** is characterized by abstraction of a phenyl radical from the molecular ion and then elimination of an HCl molecule.



REFERENCES

1. E. V. Gromachevskaya, V. G. Kul'nevich, D. P. El'chinov, T. P. Kosulina, and A. L. Chekhun, *Khim. Geterotsikl. Soedin.*, 475 (1993).
2. Lakhan Ram and R. L. Singh, *J. Prakt. Chem.*, **330**, 299 (1988).

* The values of *m/z* for the ions were calculated based on the ³⁵Cl isotope.