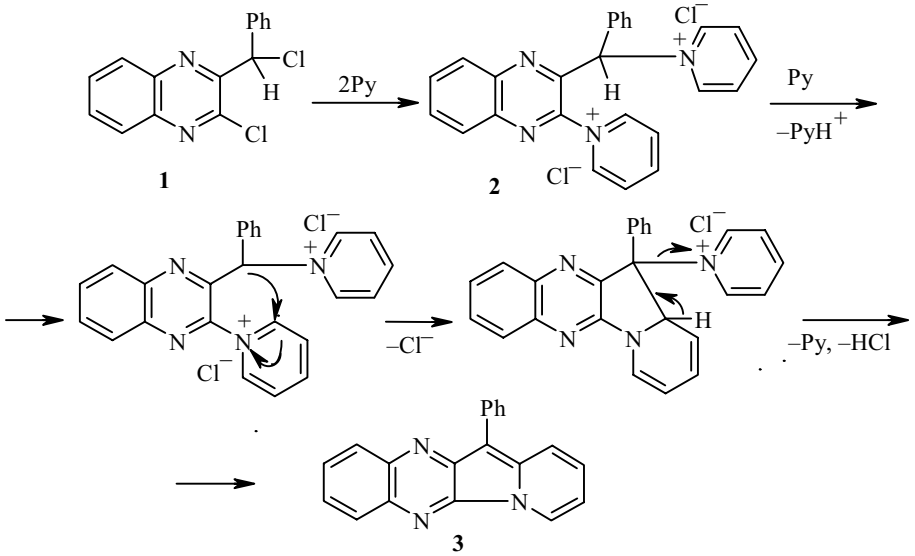
Chemistry of Heterocyclic Compounds, Vol. 36, No. 9, 2000

INTRAMOLECULAR VICARIOUS NUCLEOPHILIC SUBSTITUTION IN 2-PYRIDINIO-3-(α-PYRIDINIOBENZYL) QUINOXALINE DICATION

A. A. Kalinin, V. A. Mamedov, I. Kh. Rizvanov, and Ya. A. Levin

Keywords: intramolecular vicarious nucleophilic substitution, 2-pyridino-3-(α-pyridiniobenzyl)-quinoxaline, 12-phenylindolizino[2,3-*b*]quinoxaline, 2-chloro-3-(α-chlorobenzyl)quinoxaline.

A major limitation in the application of the vicarious nucleophilic substitution of hydrogen is the necessity of using predominantly nitro derivatives of aromatic and heterocyclic systems as the substrates [1-3]. The sequence of transformations described below may be seen as an expansion of the scope of this reaction. We have found that dipyridinium salt **2** formed from 2-chloro-3-(α-chlorobenzyl)quinoxaline (**1**) at room temperature loses a mole of pyridinium hydrochloride and HCl upon heating at reflux in pyridine and cyclizes to give 12-phenylindolizino-[2,3-*b*]quinoxaline (**3**).



1 **2** **3**

The formation of compound **3** probably involves deprotonation of the benzyl carbon atom with three electron-withdrawing groups by pyridine and subsequent nucleophilic attack of the carbanion formed on the *ortho*-carbon atom of the pyridinium substituent at $C_{(2)}$ of the quinoxaline system. This is followed by loss of pyridine from the benzyl position through a scheme analogous to vicarious nucleophilic substitution, in which the 2-pyridinium group acts as the substrate, the pyridine lost acts as the vicarium, and the substitution itself is intramolecular.

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Science Center, Russian Academy of Sciences, 420088 Kazan, Russia; e-mail: mamedov@iopc.kcn.ru. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1282-1284, September, 2000. Original article submitted May 15, 2000.

 0009-3122/00/3609-1120$25.00

2-Chloro-3-(α-chlorobenzyl)quinoxaline (1). A solution of 2-oxo-3-α-chlorobenzylquinoxaline [4] (7.05 g, 26 mmol) in $POCl_3$ (20 ml) was heated at reflux for 2 h. Excess $POCl_3$ was evaporated in vacuum and the residue was extracted with hexane (5 ×20 ml). The extract was left overnight. The crystalline precipitate was filtered off and washed with hexane (2 × 5 ml). The filtrate was evaporated and the new crystalline precipitate was filtered off and washed with hexane (2 × 3 ml). Yield 5.40 g (72%); mp 98-100°C (hexane). IR spectrum (vaseline oil), cm^{-1}: 730, 770, 782, 1045, 1120, 1260, 1445, 1565. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 6.81 (1H, s, CHPh); 7.30-8.10 (9H, m). Found, %: C 62.82; H 3.13; N 9.88; C 25.13. $C_{15}H_{10}Cl_2N_2$. Calculated, %: C 62.53; H 3.15; N 9.72; Cl 24.59.

2-α-3-Benzyldipyridinioquinoxaline Dichloride (2). A solution of dichloride **1** (0.50 g, 1.70 mmol) in pyridine (5 ml) was maintained for 96 h at room temperature. Then, hexane (20 ml) was added and stirred for 5 min. The solvent was decanted from the oily mass, which was dried in vacuum to give colorless crystals; mp 128-132°C (toluene–acetonitrile, 1:1). Yield 0.51 g (66%). IR spectrum (vaseline oil), cm^{-1}: 707, 760, 1005, 1200, 1630, 1900-3600. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 7.50-8.71 (20H, m). Found, %: C 66.81; H 4.07; Cl 15.37; N 12.28. $C_{25}H_{20}Cl_2N_4$. Calculated, %: C 67.12; H 4.51; Cl 15.85; N 12.52.

12-Phenylindolizino[2,3-*b*]quinoxaline (3). A solution of quinoxaline **2** (0.70 g, 2.40 mmol) in pyridine (5 ml) was maintained for 96 h, heated at reflux for 3 h, cooled, and poured into water. The crystalline precipitate was filtered off and washed with water to give 0.15 g (21%) of bright violet, crystalline **3**; mp 211-213°C (acetonitrile). IR spectrum (vaseline oil), cm^{-1}: 695, 755, 1135, 1440, 1510, 1617. ^1H NMR spectrum (DMSO-d_6), δ, ppm, *J* (Hz): 6.85 (1H, dd, *J* = 6.88, 6.88, H-3); 7.32 (1H, ddd, *J* = 7.73, 6.88, 1.72, H-2); 7.45 (1H, ddd, *J* = 8.60, 8.59, 2.58, H-9); 7.52-7.56 (3H, m, 2H-*m*, H-*p*); 7.76-7.82 (2H, m, H-7, H-8); 7.88 (1H, d, *J* = 7.73, H-1); 8.00-8.04 (2H, m, 2H-*o*); 8.24 (1H, ddd, *J* = 8.60, 8.59, 1.72, H-10); 9.00 (1H, br. d, *J* = 7.74, H-4). UV spectrum (in dioxane), λ_{max}, nm (log ε_{max}): 256 (4.06), 288 (4.67), 314 sh (4.17), 374 (3.88), 546 (3.42), 571 (3.45), 625 sh (3.07). Found, *m/z*: 295.112 $[M]^{+\cdot}$. $C_{20}H_{13}N_3$. Calculated: M 295.111. Found, %: C 81.56; H 4.87; N 14.12. $C_{20}H_{13}N_3$. Calculated, %: C 81.33; H 4.44; N 14.23.

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