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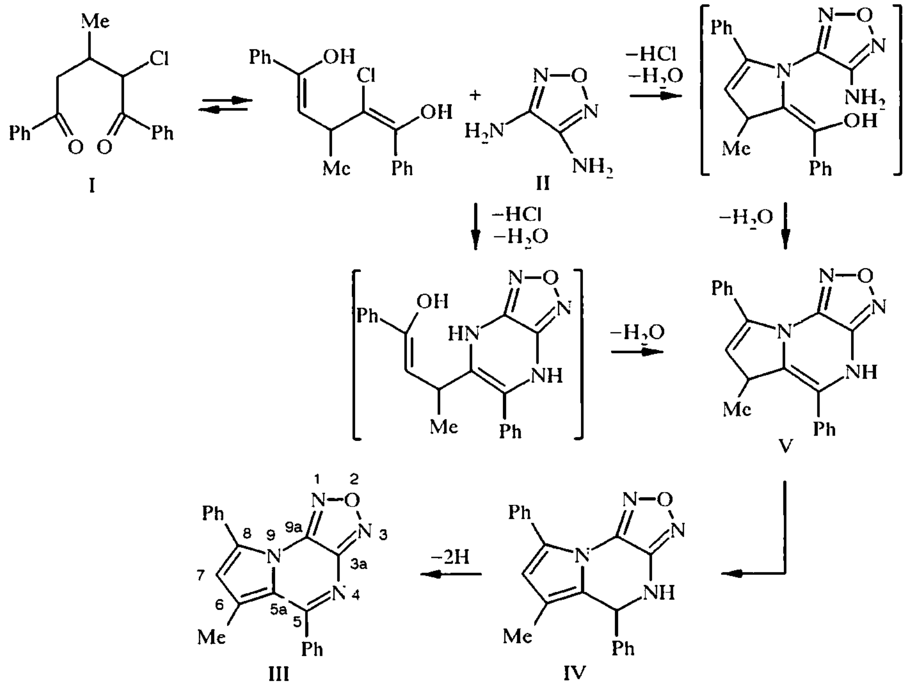
A NOVEL HETEROCYCLE, 1,2,5-OXADIAZOLO-[3,4-*e*]PYRROLO[1,2-*a*]PYRAZINE

T. V. Moskovkina and V. A. Kaminskii

We have discovered a simple synthesis of derivatives of the previously unknown heterocycle 1,2,5-oxadiazolo[3,4-*e*]pyrrolo[1,2-*a*]pyrazine *via* heating the relatively common 2-chloro-1,5-diketone (I) [1] and 3,4-diamino-1,2,5-oxadiazole (II) [2] in ethanol. The reaction products are 6-methyl-5,8-diphenyl-1,2,5-oxadiazolo[3,4-*e*]pyrrolo[1,2-*a*]pyrazine (III) and its 4,5-dihydroderivative IV. The following scheme suggests a formation path of the tricyclic system III (or IV):



Closing first the pyrrole and then the pyrazine ring or, conversely, first the pyrazine and then the pyrrole ring, apparently gives the same product V. Migration of the double bond in V from the pyrazine to the pyrrole ring gives the dihydrocompound IV. A migration of the same type with a shift of a double bond from a pyrazine to a pyrrole ring was noted previously during the preparation of pyrrolo[1,2-*a*]quinoxalines from α-oxy-1,5-diketones and *o*-phenylenediamine [3]. We demonstrated that IV is readily dehydrogenated by MnO_2 to give the aromatic system III. The dehydrogenation obviously also occurs during the reaction because the compound III is the main product and the dihydroderivative IV appears as an impurity. The structures of compounds III and IV were confirmed by IR, mass, and NMR spectra.

Far-East State University, Vladivostok 690600, Russia; e-mail: stonik@piboc.marine.su. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 1002-1003, July, 1999. Original article submitted April 27, 1999.

Synthesis of Compounds III and IV. To a solution of diketone I (0.6 g, 2 mmol) in boiling ethanol (15 ml) the oxadiazole II (0.2 g, 2 mmol) was added. The reaction mixture was boiled for 2 h, evaporated to half the initial volume, and cooled in an ice bath. The resulting precipitate is filtered off. Yield 0.4 g (60%) of III. The solvent was removed from the mother liquor under vacuum and the residue was chromatographed on silica gel L (100-250 μ). Compound III (0.07 g, 10%) was eluted with petroleum ether; compound IV (0.1 g, 15%), with a petroleum ether–ethylacetate (3:5) mixture.

Oxidation of Compound IV by MnO_2. A solution of IV (0.05 g, 0.015 mmol) in ether was treated with activated MnO_2 (0.1 g). The reaction mixture was stirred for 3 h. The solution was filtered. The filtrate was evaporated and the residue was recrystallized from ethanol. Yield 0.03 g (60%) of III with an IR spectrum identical to that of a previously prepared sample of III.

5,8-Diphenyl-6-methyl-1,2,5-oxadiazolo[3,4-*e*]pyrrolo[1,2-*a*]pyrazine (III). Yield 75%; mp 210-211°C. IR spectrum ($CHCl_3$): 1612 cm^{-1} (C=N). Mass spectrum, *m/z*: 326 $[M^+]$. ^1H NMR spectrum (250 MHz, $CDCl_3$): 1.90 (3H, s, CH_3); 6.67 (1H, s, 7-H); 7.50-7.72 ppm (10H, m, 2Ph). ^{13}C NMR spectrum ($CDCl_3$): 14.5 (CH_3), 119.5 ($C_{(7)}$), 128.4, 129.0, 129.6, 130.2 (10CH, 2 Ph), 123.8, 128.9, 129.3, 137.4, 137.8, 142.5, 152.8, 163.9 ppm (8C). Found, %:C 73.60; H 4.24; N 17.10. $C_{20}H_{14}N_4O$. Calculated, %: C 73.68; H 4.29; N 17.18.

4,5-Dihydro-5,8-diphenyl-6-methyl-1,2,5-oxadiazolo[3,4-*e*]pyrrolo[1,2-*a*]pyrazine (IV). Yield 15%; mp 168-170°C. IR spectrum ($CHCl_3$): 3368 cm^{-1}. Mass spectrum, *m/z*: 328 $[M^+]$. ^1H NMR spectrum (250 MHz, $CDCl_3$): 1.90 (3H, s, CH_3); 5.15 (1H, s, NH); 5.77 (1H, s, $H_{(5)}$); 6.25 (1H, s, $H_{(7)}$); 7.50-7.72 ppm (10H, m, 2Ph). Found, %: C 73.10; H 4.77; N 16.94. $C_{20}H_{16}N_4O$. Calculated, %: C 73.17; H 4.87; N 17.07.

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