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LETTERS TO THE EDITOR

CYCLIZATION OF 4-[ALKOXYCARBONYL-METHYLAMINO]- AND 4-[ALKOXYCARBONYL-METHYLTHIO]-5-AMINOPYRROLO[2,3-*d*]-PYRIMIDINES TO GIVE AZABENZ[*cd*]AZULENES

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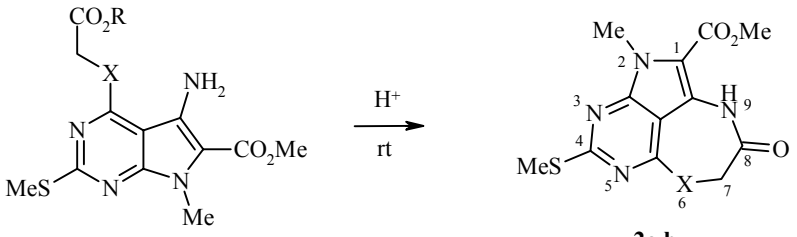
Keywords: heterocycles, 2H-2,3,5,6,9-pentaazabenz[*cd*]azulene, pyrrolo[2,3-*d*]pyrimidine, 6-thia-2,3,5,9-tetraazabenz[*cd*]azulene, cyclocondensation.

In a recent communication [1], we reported a synthesis for 2,3,5,6,9-pentaazabenz[*cd*]azulene, involving acetylation of the methyl ester of 5-amino-4-(ethoxycarbonylmethylamino)-7-methyl-2-methylthiopyrrolo-[2,3-*d*]pyrimidine-6-carboxylic acid (**1a**) using chloroacetyl chloride and subsequent condensation of the 5-chloroacetylaminopyrrolopyrimidine formed using K_2CO_3/DMF. In a continuation of this study, we have found that **1a** and **1b** cyclize in the presence of a catalytic amount of acid to give the corresponding *peri*-condensed heterocyclic systems **2a** and **2b**.



1a,b **2a,b**

a R = Et, X = NH; **b** R = Me, X = S

The spectral data for **2a** and **2b** are in good accord with the proposed structures.

The present method for the synthesis of 6,7,8,9-tetrahydro-2H-2,3,5,6,9-pentaaza- and 2,7,8,9-tetrahydro-6-thia-2,3,5,9-tetraazabenz[*cd*]azulenes is an alternative to our previous method [1] and may be used for the synthesis of derivatives of these compounds containing substituents sensitive to bases.

The IR spectra were taken on a Perkin–Elmer Spectrum BX II FT-IR in vaseline oil. The ^{1}H NMR spectra were taken on a Tesla BS-587A spectrometer at 80 MHz in DMSO-d_6 with TMS as the internal standard.

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Methyl Ester of 2-Methyl-4-methylthio-8-oxo-6,7,8,9-tetrahydro-2H-2,3,5,6,9-pentaazabenz[*cd*]-azulene-1-carboxylic Acid (2a). Two drops of concentrated hydrochloric acid was added to a solution of **1a** (0.1 g, 0.28 mmol) [2] in chloroform (15 ml). The reaction mixture was stirred at room temperature for 1.5 h and methanol (10 ml) was added. The precipitate was filtered off and dissolved in hot DMSO. Then, 25% aq. ammonia was added to bring the solution to pH 8. The precipitate formed was filtered off and washed with water to give 0.03 g (33%) of compound **2a**; mp >290°C (dec., DMF). IR spectrum, ν, cm^{-1}: 3305 (NH), 3212 (NH), 1711 (CO), 1763 (CO). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.54 (3H, s, SCH_3); 3.85 (3H, s, NCH_3); 3.90 (3H, s, OCH_3); 4.05 (2H, d, *J* = 3.5, NCH_2); 8.14 (1H, br. t, *J* = 7.0, NH); 9.52 (1H, s, NH). Found, %: C 47.05; H 4.54; N 22.68. $C_{12}H_{13}N_4O_3S$. Calculated, %: C 46.90; H 4.26; N 22.79.

Methyl Ester of 2-Methyl-4-methylthio-8-oxo-2,7,8,9-tetrahydro-6-thia-2,3,5,9-tetraazabenz[*cd*]-azulene-1-carboxylic Acid (2b). A drop of concentrated sulfuric acid was added to a solution of (0.17 g, 0.48 mmol) **1b** [2] in dichloromethane (15 ml). The reaction mixture was filtered off, washed with water, and recrystallized to give 0.05 g (32%) of compound **2b**; mp 199-202°C (2-propanol). IR spectrum, ν, cm^{-1}: 3332 (NH), 1687 (CO), 1673 (CO). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.52 (3H, s, SCH_3); 3.89 (6H, s, NCH_3, OCH_3); 3.98 (2H, s, SCH_2); 9.65 (1H, s, NH). Found, %: C 44.70; H 3.84; N 17.35. $C_{12}H_{12}N_4O_3S_2$. Calculated, %: C 44.43; H 3.73; N 17.27.

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2. S. Tumkevicius, Z. Sarakauskaite, and V. Masevicius, *Synthesis*, in press.