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FORMATION OF 2-ARYL-5-METHYL-7,8-DIMETHOXYBENZO[*d*]PYRROLO-[3,2-*b*]PYRILIUM PERCHLORATES AS THE RESULT OF TANDEM HETERO-CYCLIZATION IN THE ACYLATION OF 2-(3,4-DIMETHOXYPHENYL)-4-OXO-4-ARYLBUTYRONITRILES

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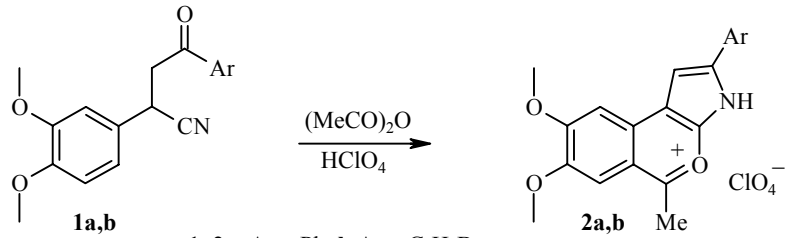
In a study of the acylation of 4-aryl-2-(3,4-dimethoxyphenyl)-4-oxobutyronitriles (**1a,b**) in a mixture of 70% perchloric acid and acetic anhydride, we found that tandem reactions yield a new heterocyclic system, namely, 2-aryl-5-methyl-7,8-dimethoxybenzo[*d*]pyrrolo[3,2-*b*]pyrilium perchlorates (**2a,b**).



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

1, 2 a Ar = Ph, **b** Ar = C_6H_4Br-*p*

This reaction involves acylation of the veratrol fragment and subsequent heterocyclization to give pyrilium and pyrrole rings. The structures of cyclization products **2a** and **2b** were confirmed by ^{1}H NMR spectroscopy. The assignment of the chemical shifts of the pyrrole and veratrol rings was carried out using the 2M COSY technique.

7,8-Dimethoxy-5-methyl-2-phenylbenzo[*d*]pyrrolo[3,2-*b*]pyrilium Perchlorate (2a). Keto nitrile **1a** (3 g, 0.01 mol) was added with stirring to an acylating mixture consisting of acetic anhydride (10 ml) and 70% perchloric acid (2 ml) cooled to 5°C. The mixture was stirred for 1 h and kept for night at room temperature. The precipitate of pyrilium salt **2a** was filtered off and washed consecutively with acetic acid, 2-propanol, and ether to give 3 g (71%) **2a**; mp 298-299°C (acetic acid). ^{1}H NMR spectrum (DMSO-d_6 + CF_3CO_2H), δ, ppm,

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J (Hz): 2.91 (3H, s, 5-CH_3); 3.97 (3H, s, 7-OCH_3); 4.03 (3H, s, 8-OCH_3); 7.41 (1H, t, 4'-H); 7.49 (1H, s, 6-H); 7.48-7.59 (2H, m, 3'- and 5'-H); 7.68 (1H, s, 9-H); 7.91 (2H, d, *J* = 8, 2'- and 6'-H); 7.96 (1H, s, 1-H). Found, %: C 57.44; H 4.23; Cl 8.65; N 3.44. $C_{20}H_{18}ClNO_7$. Calculated, %: C 57.22; H 4.32; Cl 8.44; N 3.34.

2-(4'-Bromophenyl)-5-methyl-7,8-dimethoxybenzo[*d*]pyrrolo[3,2-*b*]pyrilium Perchlorate (2b) was obtained in 70% yield analogously to **2b** from 2-(3,4-dimethoxyphenyl)-4-oxo-4-(4'-bromophenyl)butyronitrile (**1b**); mp >350°C (acetic acid). ^{1}H NMR spectrum (DMSO-d_6 + CF_3CO_2H), δ, ppm, *J* (Hz): 2.99 (3H, s, 5-CH_3); 3.79 (3H, s, 7-OCH_3); 3.96 (3H, s, 8-OCH_3); 7.24 (1H, s, 6-H); 7.27 (2H, d, *J* = 7.8, 3'- and 5'-H); 7.31 (1H, s, 9-H); 7.50 (2H, d, *J* = 7.8, 2'-, 6'-H); 8.50 (1H, s, 1-H). Found, %: C 48.38; H 3.23; Br 16.19; Cl 7.00; N 2.74. $C_{20}H_{17}BrClNO_7$. Calculated, %: C 48.17; H 3.44; Br 16.02; Cl 7.11; N 2.81.