ISSN 1070-4280, Russian Journal of Organic Chemistry, 2006, Vol. 42, No. 4, pp. 622–623. © Pleiades Publishing, Inc., 2006.
Original Russian Text © E.A. Melekhin, I.N. Bardasov, O.V. Ershov, A.V. Eremkin, Ya.S. Kayukov, O.E. Nasakin, 2006, published in Zhurnal Organicheskoi Khimii, 2006, Vol. 42, No. 4, pp. 639–640.

SHORT COMMUNICATIONS

Synthesis of 5-Aryl-2,4-diamino-8-hydroxy-5*H*-chromeno[2,3-*b*]pyridine-3-carbonitriles

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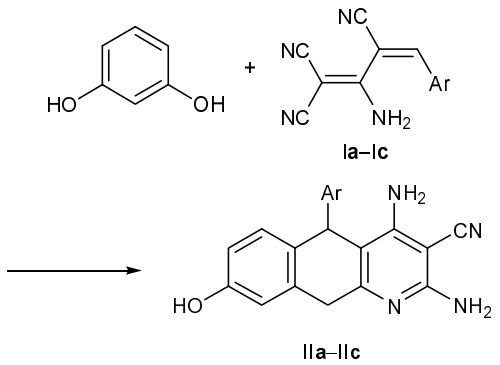
Received November 7, 2005

DOI: 10.1134/S1070428006040269

α,β-Unsaturated alcohols are known to react with electron-rich phenols with formation of 2-amino-4*H*-chromenes [1, 2]. Some 2-amino-4*H*-chromenes were found to exhibit biological activity [3–6]; in particular, they can be used as immunomodulators and in the prophylactics and treatment of various connective tissue disorders, diabetes, psoriasis, malignant anemia, ulcerative colitis, chronic hepatitis, etc. [3].

With the goal of synthesizing new 2-chromene derivatives, in the present work we used 2-amino-4-arylbuta-1,3-diene-1,1,3-tricarbonitriles **Ia**–**Ic** (arylmethylidene derivatives of malononitrile dimer) whose reactions with phenols were not described previously. We have found that compounds **Ia**–**Ic** react with resorcinol to give the corresponding 10-aryl-2,4-diamino-7-hydroxy-10*H*-9-oxa-1-azaanthracene-3-carbonitriles **IIa**–**IIc** as a result of a series of transformations. The structure of products **IIa**–**IIc** was confirmed by the IR, ^{1}H NMR and mass spectra.

2,4-Diamino-8-hydroxy-5-(3-nitrophenyl)-5*H*-chromeno[2,3-*b*]pyridine-3-carbonitrile (IIa).



Ar = 3-$O_2NC_6H_4$ (**a**), 4-$Me_2NC_6H_4$ (**b**), 4-FC_6H_4 (**c**).

Resorcinol, 1.1 g (10 mmol), and a catalytic amount of piperidine were added to a solution of 2.65 g (10 mmol) of 2-amino-4-(3-nitrophenyl)buta-1,3-diene-1,1,3-tricarbonitrile (**Ia**) in 150 ml of ethanol. The mixture was heated for 12 h under reflux and cooled, and the precipitate was filtered off and recrystallized from ethanol. Yield 2.92 g (78%), mp 288–289°C. IR spectrum, ν, cm^{-1}: 3150–3500 (NH_2), 2210 (C≡N). ^{1}H NMR spectrum, δ, ppm: 5.4 s (1H, 5-H), 6.52 s (2H, NH_2), 6.53 s (2H, NH_2), 6.54 s (1H, phenol), 6.55 d (1H, phenol), 6.99 d (1H, phenol), 7.55 t (1H, H_{arom}), 7.62 d (1H, H_{arom}), 8.02 d (1H, H_{arom}), 8.2 s (1H, H_{arom}), 9.68 s (1H, OH). Mass spectrum, *m*/z (I_{rel}, %): 375 (11.2), 253 (100). Found, %: C 60.76; H 3.46; N 18.72. $C_{19}H_{13}N_5O_4$. Calculated, %: C 60.80; H 3.49; N 18.66.

Compounds **IIb** and **IIc** were synthesized in a similar way.

2,4-Diamino-5-(4-dimethylaminophenyl)-8-hydroxy-5*H*-chromeno[2,3-*b*]pyridine-3-carbonitrile (IIb). Yield 2.53 g (68%), mp 284–286°C. IR spectrum, ν, cm^{-1}: 3150–3500 (NH_2), 2220 (C≡N). ^{1}H NMR spectrum, δ, ppm: 4.98 s (1H, 5-H), 6.1 s (2H, NH_2), 6.26 s (2H, NH_2), 6.44 s (1H, phenol), 6.46 d (1H, phenol), 6.58 d (2H, H_{arom}), 6.93 d (1H, H_{arom}), 7.11 d (2H, H_{arom}), 9.48 s (1H, OH). Mass spectrum, *m*/z (I_{rel}, %): 373 (14.5), 253 (100). Found, %: C 67.51; H 5.15; N 18.78. $C_{21}H_{19}N_5O_2$. Calculated, %: C 67.55; H 5.13; N 18.76.

2,4-Diamino-5-(4-fluorophenyl)-8-hydroxy-5*H*-chromeno[2,3-*b*]pyridine-3-carbonitrile (IIc). Yield 2.54 g (73%), mp 292–294°C. IR spectrum, ν, cm^{-1}: 3150–3500 (NH_2), 2210 (C≡N). ^{1}H NMR spectrum, δ,

ppm: 5.19 s (1H, 5-H), 6.36 s (2H, NH_2), 6.44 s (2H, NH_2), 6.46 s (1H, phenol), 6.47 d (1H, phenol), 6.96 d (1H, phenol), 7.06 t (2H, H_{arom}), 7.24 d (1H, H_{arom}), 7.26 d (1H, H_{arom}), 9.6 s (1H, OH). Mass spectrum, *m*/z (I_{rel}, %): 348 (19.9), 253 (100). Found, %: C 65.58; H 3.72; N 16.13. $C_{19}H_{13}FN_4O_2$. Calculated, %: C 65.51; H 3.76; N 16.08.

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