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AN UNUSUAL REACTION OF (2-OXO-1,2-DIHYDRO-3H-INDOL-3-YLIDENE)ACETIC ACID ESTERS WITH HYDRAZINE

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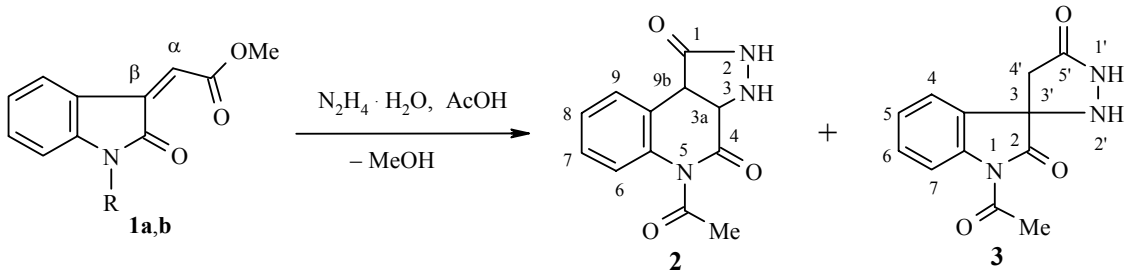
Keywords: 5-acetyl-3,3a,5,9b-tetrahydro-1H-pyrazolo[3,4-*c*]quinoline-1,4(2H)-dione, 1-acetyl-5'H-spiro[indole-3,3'-pyrazolidine]-2,5'(1H)-dione, (2-oxo-1,2-dihydro-3H-indol-3-ylidene)acetic acid esters, reaction with hydrazine.

The reaction of 3-(2-oxo-2-(alkyl)(het)arylethylidene)-1,3-dihydro-2H-indol-2-ones with hydrazine or phenylhydrazine under mild conditions leads to formation of 2',4'-dihydrospiro[indole-3,3'-pyrazol]-2(1H)-ones [1-4]. In this case, the amino group of the hydrazine is added at the β-position of the 3-exocyclic C–C double bond of the substrate. Recently in a study of the reaction of (2-oxo-1,2-dihydro-3H-indol-3-ylidene)acetic acid esters with phenylhydrazine, the products of chemoselective addition of a nucleophile at the α-position of the double bond (vicinal hydrazine derivatives) were unexpectedly obtained: (2-oxo-2,3-dihydro-1H-indol-3-yl)-2-phenylhydrazinoacetic acid esters [5]. For the first time, we have established that treatment of (2-oxo-1,2-dihydro-3H-indol-3-ylidene)acetic acid methyl esters **1a,b** with hydrazine hydrate, when the mixture is boiled in acetic acid, mainly leads to formation of the product of addition at the α-position of the 3-*exo* C–C double bond (followed by recyclization): 5-acetyl-3,3a,5,9b-tetrahydro-1H-pyrazolo[3,4-*c*]quinoline-1,4(2H)-dione (**2**), but results in formation of 1-acetyl-5'H-spiro[indole-3,3'-pyrazolidine]-2,5'(1H)-dione (**3**) (the β-addition product) in only insignificant yields (6%-12%).



1a,**b** **2** **3**

1 a R = H, **b** R = MeCO

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Reaction of (2*Z*)-(2-Oxo-1,2-dihydro-3H-indol-3-ylidene)acetic Acid Methyl Esters with Hydrazine Hydrate. A mixture of (2*Z*)-(2-oxo-1,2-dihydro-3H-indol-3-ylidene)acetic acid methyl ester **1a** (1.01 g, 0.005 mol) or the N-acetyl derivative **1b** (1.23 g, 0.005 mol) and a 70% aqueous solution of hydrazine (0.3 ml) in acetic acid (50 ml) was boiled for 2.5-3 h. The solvent was evaporated, the residue was recrystallized from 2-propanol (spiro compound **3** was isolated) and acetic acid (compound **2** was obtained).

5-Acetyl-3,3a,5,9b-tetrahydro-1H-pyrazolo[3,4-*c*]quinoline-1,4(2H)-dione (2). Yield 0.72 g (59%) (from starting compound **1a**) and 0.87 g (71%) (from compound **1b**); mp 275-276°C (decomposes, from AcOH). ^{1}H NMR spectrum (500 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 2.13 (3H, s, CH_3 in MeCO); 4.41 (1H, d, *J* = 18.5, H-3a); 5.57 (1H, d, H-9b); 6.90 (1H, d, H-9); 7.02 (1H, t, H-7); 7.23 (1H, t, H-8); 7.25 (1H, d, H-6); 10.60 (1H, br. s, H-2); 11.30 (1H, br. s, H-3). Mass spectrum, *m/z* (I_{rel}, %): 245 $[M]^+$ (9), 204 (8), 203 $[M–CH_2CO]^+$ (72), 147 (9), 146 $[M–CH_3CO–N_2–CO]^+$ (100), or a tetrahydroquinolone fragment $[C_9H_8NO]^+$, 145 $[C_9H_7NO]^+$ (92), 144 (17), 128 (20), 117 (32), 104 (5), 90 (16), 89 (15), 77 $[C_6H_5]^+$ (8), 63 (7), 51 (5), 43 $[CH_3CO]^+$ (49). Found, %: C 58.77; H 4.52; N 17.13. $C_{12}H_{11}N_3O_3$. Calculated, %: C 59.02; H 4.36; N 16.87.

1-Acetyl-5'H-spiro[indole-3,3'-pyrazolidine]-2,5'(1H)-dione (3). Yield 0.07 g (6%) (from starting compound **1a**) and 0.15 g (12%) (from compound **1b**); mp 188-189°C (with decomposition, from 2-propanol). ^{1}H NMR spectrum (500 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 2.15 (3H, s, CH_3 in MeCO); 3.96, 4.27 (2H, 2d, *J* = 15.8, 2H-4'); 6.87 (1H, d, H-4); 6.98 (1H, t, H-6); 7.18 (1H, t, H-5); 7.22 (1H, d, H-7); 9.32 (1H, br. s, H-1'); 10.31 (1H, br. s, H-2'). Found, %: C 58.77; H 4.52; N 17.13. $C_{12}H_{11}N_3O_3$. Calculated, %: C 58.51; H 4.68; N 17.37.

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