RECYCLIZATION OF THE PYRROLE RING TO A PYRAZOLE RING IN THE REACTION OF 4-ACYL-2,3-DIHYDROPYRROLE-2,3-DIONE WITH ARYLHYDRAZINES

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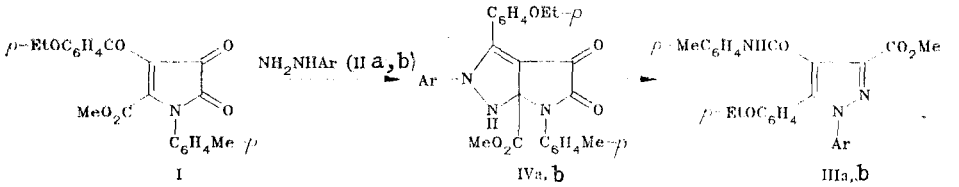
4-Unsubstituted, 4-alkyl-, and 4-phenyl-2,3-dihydropyrrole-2,3-diones react with arylhydrazines to give (Z)-3-arylhydrazones (for example, see [1]). We unexpectedly isolated substituted pyrazole-4-glyoxamides IIIa, b in the reaction of 4-acyl-2,3-dihydropyrrole-2,3-dione I with arylhydrazines IIa, b.



I IVa, b IIIa, b

II—IV a Ar=Ph, b Ar=*p*-MeC_6H_4

The reaction evidently proceeds through a step involving the addition of the primary amino group of IIa, b to the $C_{(5)}$ atom of 4-acylpyrroledione I, as described for the reaction with amines [2], and addition of the secondary amino group to the carbonyl group of the 4-acyl substituent and dehydration to give pyrrolo[2,3-c]pyrazoles IVa, b. The latter undergo cleavage of the pyrrole ring at the $N—C_{(5)}$ bond with a [1,3]-prototropic shift, probably as a consequence of the strained character of the system from two condensed five-membered heterorings and the ease of cleavage of the C—N bond in gem-diamines.

3-Methoxycarbonyl-N-(p-tolyl)-1-phenyl-5-(p-ethoxyphenyl)-1H-pyrazole-4-glyoxamide(IIIa). A solution of 0.01 mole of I and 0.01 mole of phenylhydrazine (IIa) in 20 ml of chloroform was heated up to the boiling point, after which it was cooled to give 3.24 g (67%) of IIIa with mp 190-192°C (from methanol). IR spectrum (mineral oil): 3320 (NH); 1751 (COO); 1692 [$C_{(4)}$—C=O]; 1680 (CONH); 1612, 1600 (C=N, C=O); 1537 cm^{-1} (amide II). PMR spectrum ($CDCl_3$): 1.33 (3H, t, CH_3), 2.25 (3H, s, CH_3), 3.83 (3H, s, CH_3O), 4.00 (2H, q, CH_2O), 6.63-7.74 (13H, m, $2C_6H_4$, C_6H_5), 8.70 ppm (1H, s, NH). Mass spectrum, m/z (I_{rel}, %): 483 (6) [$M^{+\cdot}$], 349 (100) [M − $CONHC_6H_4Me$-p], 321 (5) [M − $COCONHC_6H_4Me$-p], 291 (6) [M − $COOMe$-p-MeC_6H_4NCO], 196 (6), 77 (16).

3-Methoxycarbonyl-N,1-di(p-tolyl)-5-(p-ethoxyphenyl)-1H-pyrazole-4-glyoxamide (IIIb). A similar procedure gave 3.08 g (62%) of IIIb with mp 190-192°C (from ethanol). IR spectrum: 3308 (NH); 1745 (COO); 1695 [$C_{(4)}$—C=O]; 1678 (CONH); 1611, 1592 (C=N, C=C); 1535 cm^{-1} (amide II). PMR spectrum (d_6-DMSO): 1.27 (3H, t, CH_3), 2.25 (6H, s, $2CH_3$), 3.70 (3H, s, CH_3O), 3.98 (2H, q, CH_2O), 6.71-7.78 (12H, m, $3C_6H_4$), 10.61 ppm (1H, s, NH).

The results of elementary analysis of IIIa, b were in agreement with the calculated values.

LITERATURE CITED

1. L. Capuano and P. Mörsdorf, Ann., No. 9, 2178 (1982).
2. A. N. Maslivets, L. I. Smirnova, and Yu. S. Andreichikov, Zh. Org. Khim., **25**, 1748 (1989).

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