SYNTHESIS OF BENZENE-RING-SUBSTITUTED 2-METHYL-3-ACETYLQUINOXALINE DERIVATIVES

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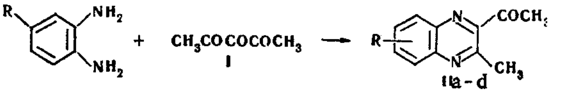
2-Methyl-4-acetylquinoxaline derivatives were obtained by the condensation of pentane-2,3,4-trione with 4-substituted o-phenylenediamines.

We applied the previously described [1,2] reaction of vicinal tricarbonyl compounds with o-phenylenediamine to 4-substituted o-phenylenediamines to obtain benzene-ring-substituted 2-acetyl-3-methylquinoxalines (IIa-d):



IIa R = H; IIb R = 7-CH_3; IIc R = 6-NO_2; IId R = 7-NH_2

This reaction can result in the formation of a mixture of 6 and 7 derivatives, but, according to the spectral data and the results of thin-layer chromatography, only one isomer is formed in all cases. The stereospecificity of the reaction and the orienting effect of the substituents in the 4 position of o-phenylenediamine derivatives were noted in [3], in which 2-methyl-6-nitroquinoxaline and 2-methyl-7-aminoquinoxaline, respectively, were obtained by the reaction of methylglyoxal with 4-nitro- and 4-amino-o-phenylenediamine. The structures of the compounds obtained by the authors were proved unambiguously by alternative synthesis. Assuming that in our case we are dealing with a similar orientation of the addition reaction, we assigned the structures of 7-methyl-, 6-nitro-, and 7-amino derivatives of 2-methyl-3-acetylquinoxaline to IIb-d.

An intense absorption band at 1700 cm^{-1}, caused by vibrations of the conjugated carbonyl group, is observed in the IR spectra of IIa-d. The UV spectra (IIb, λ_{max} 250 and 325 nm, $\log \varepsilon$ 4.54 and 3.99; IIc, λ_{max} 265 and 325 nm, $\log \varepsilon$ 4.47 and 3.74; IId, λ_{max} 230, 290, and 405 nm, $\log \varepsilon$ 4.34, 4.28, and 4.13) are in agreement with data previously presented for similar systems [4].

EXPERIMENTAL

2-Methyl-3-acetyl-7-aminoquinoxaline (IId). A solution of 2.3 g (0.02 mole) of I in 10 ml of alcohol and a solution of 4 g (0.02 mole) of 1,2,4-triaminobenzene hydrochloride in 15 ml of water were refluxed for 1.5 h with a catalytic amount of sodium acetate and allowed to stand overnight. The precipitate was treated with 5% sodium carbonate solution and extracted with ether to give 1.8 g (44%) of IId with mp 233-234° (from alcohol). Found: C 65.8; 66.0; H 5.5; 5.7; N 20.4, 20.5%. $C_{11}H_{11}N_3O$. Calculated: C 65.7; H 5.5; N 20.9%.

Compounds IIa-c were similarly obtained.

2-Methyl-3-acetylquinoxaline (IIa). This compound had mp 86-87° (from water–alcohol) (mp 86.5° [5]).

2,7-Dimethyl-3-acetylquinoxaline (IIb). This compound had mp 91-92° (from water–alcohol). Found: C 72.2, 72.0; H 6.1, 6.0; N 14.2, 14.3%. $C_{12}H_{12}N_2O$. Calculated: C 72.0; H 6.0; N 14.0%. The 2,4-Dinitrophenylhydrazone was obtained as yellow crystals with mp 230-232° (from dimethylformamide–alcohol). Found: C 57.2; H 4.5; N 22.2%. $C_{18}H_{16}N_6O_4$. Calculated: C 56.8; H 4.2; N 22.1%.

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2-Methyl-3-acetyl-6-nitroquinoxaline (IIc). This compound had mp 138.5-139° (from alcohol). Found: C 56.7, 56.7; H 4.0, 4.0; N 18.4, 18.3%. $C_{11}H_9N_3O_3$. Calculated: C 57.1; H 3.9; N 18.2%.

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