ACYLQUINOXALINES

III.* STRUCTURES OF THE PRODUCTS OF CONDENSATION OF SUBSTITUTED o-PHENYLENEDIAMINE WITH DIMETHYL TRIKETONE (2,3,4-PENTANETRIONE)

V. V. Titov and L. F. Kozhokina

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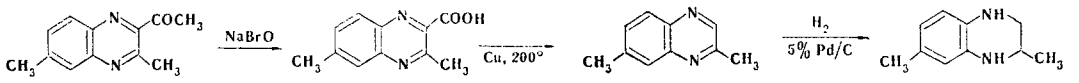
The structure of 2,7-dimethyl-3-acetylquinoxaline was proved by conversion of it to 2,7-dimethyl-1,2,3,4-tetrahydroquinoxaline. 2,7-Dimethylquinoxaline and 2-methyl-3-acetyl-6-aminoquinoxaline were synthesized.

The condensation of 4-substituted o-phenylenediamines with unsymmetrical α-diketones or vicinal triketones can give 6- or 7-substituted quinoxaline derivatives as well as mixtures of them. It has been shown [2] that the condensation of 4-R-o-phenylenediamine with dimethyl triketone (2,3,4-pentanetrione) gives individual products which, considering the orienting effect of substituents in o-phenylenediamine and the similarity to analogous transformations of methylglyoxal [3], were assigned 2,7-dimethyl-3-acetylquinoxaline,2-methyl-3-acetyl-7-aminoquinoxaline, and 2-methyl-3-acetyl-6-nitroquinoxaline structures.



I II III IV

In the present paper, the 2,7-dimethyl-3-acetylquinoxaline (I) structure was proved by conversion of I to the known 2,7-dimethyl-1,2,3,4-tetrahydroquinoxaline (IV) via the scheme shown above. The latter was synthesized from 3-amino-4-nitrotoluene via the method in [4].

The oxidation of I with sodium hypobromite gave the previously undescribed 2,7-dimethylquinoxaline-3-carboxylic acid (II), the decarboxylation of which gives 2,7-dimethylquinoxaline (III), which previously had been obtained only in a mixture with the isomeric 2,6-dimethylquinoxaline [4,5].

The catalytic hydrogenation of III yielded 2,7-dimethyl-1,2,3,4-tetrahydroquinoxaline (IV), which proved to be identical to the previously described product with respect to its melting point, thin-layer chromatography data, and UV spectrum (λ_{max} 255 and 315 nm; log ε 3.69 and 3.61).

Reduction of 2-methyl-3-acetyl-6-nitroquinoxaline with sodium hydrosulfite gave 2-methyl-3-acetyl-6-aminoquinoxaline, which differed from the previously synthesized isomer [1] (see Fig. 1). Thus it was confirmed that the amino and nitro groups are in different positions in the corresponding 2-methyl-3-acetylquinoxaline derivatives.

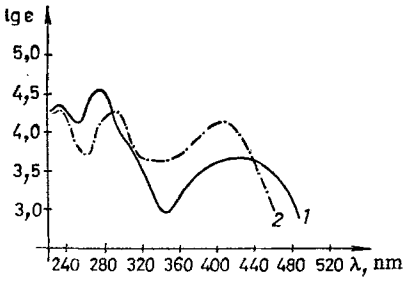


Fig. 1. UV spectra in alcohol: 1) 2-methyl-3-acetyl-6-aminoquinoxaline; 2) 2-methyl-3-acetyl-7-aminoquinoxaline.

*See [1] for communication II.

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EXPERIMENTAL

2,7-Dimethylquinoxaline-3-carboxylic Acid (II). A solution of 0.8 g (4 mmole) of I in 10 ml of dioxane was added dropwise in the course of 30 min to a solution of sodium hypobromite, prepared from 2.4 g (0.06 mole) of NaOH in 11.5 ml of water and 0.86 ml (0.032 mole) of bromine at 0°. The mixture was stirred at 30-40° for 30 min, after which the excess hypobromite was removed by the addition of sodium bisulfite solution. The mixture was then diluted with 10 ml of water, and the dioxane and bromoform were removed by vacuum distillation. The mixture was then acidified and filtered to give 0.55 g (68%) of II with mp 156.5-157.5° (from alcohol). Found,%: C 65.1; H 5.0; N 14.1. $C_{11}H_{10}N_2O_2$. Calculated,%: C 65.3; H 5.0; N 13.9. An intense band at 1710 cm^{-1} (ν CO) was observed in the IR spectrum of II.

2,7-Dimethylquinoxaline (III). A 0.32-g (1.6 mmole) sample of II was added to 10 ml of ethylene glycol containing a catalytic amount of copper powder, and the mixture was refluxed for 1.5 h on a silicone bath. It was then cooled and extracted with petroleum ether to give 0.15 g (61%) of III with mp 74-75° (from petroleum ether). Found,%: C 76.2; H 6.4; N 17.4. $C_{10}H_{10}N_2$. Calculated,%: C 75.9; H 6.4; N 17.7. UV spectrum in cyclohexane: λ_{max} 320 nm (log ε 3.809).

2,7-Dimethyl-1,2,3,4-tetrahydroquinoxaline (IV). A Wilkinson–Ferry apparatus was charged with 0.12 g (0.76 mmole) of III in 10 ml of absolute alcohol and 0.06 g of 5% Pd/C, and the mixture was refluxed for 4 h with simultaneous admission of hydrogen. The mixture was then filtered, and the filtrate was evaporated to give 0.11 g (89%) of IV with mp 117-118° (from benzene–petroleum ether) (mp 118-118.5° [4]). Found,%: C 74.0; H 8.5; N 17.3. $C_{10}H_{14}N_2$. Calculated,%: C 74.0; H 8.7; N 17.3.

6-Amino-2-methyl-3-acetylquinoxaline. A solution of 0.41 g (1.8 mmole) of 6-nitro-2-methyl-3-acetylquinoxaline in 20 ml of alcohol was refluxed with a solution of 2.1 g (0.01 mole) of sodium hydrosulfite in 7 ml of water for 30 min. The mixture was then filtered, and the filtrate was extracted with ether to give 0.24 g (68%) of 6-amino-2-methyl-3-acetylquinoxaline with mp 151-152° (purified by crystallization from benzene–petroleum ether and subsequent sublimation). Found,%: C 66.0; H 5.5; N 21.0. $C_{11}H_{11}N_3O$. Calculated,%: C 65.7; H 5.5; N 20.8.

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