ACYLQUINOXALINES

II.* SYNTHESIS OF 3-PHENYL- AND 3-METHYL-2,2-DIQUINOXALYLS

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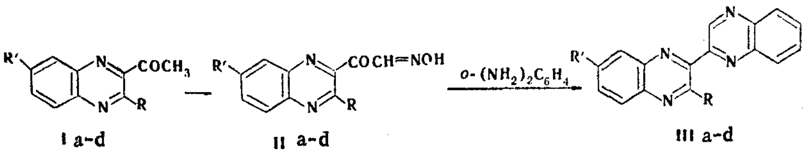
3-Phenyl-2,2'-diquinoxalyls and 7-substituted 3-methyl-2,2'-diquinoxalyls were obtained by the condensation of 2-quinoxalylglyoxal monooximes with o-phenylenediamine.

In the course of a search for organic compounds that have high photoconductivity, we synthesized unsymmetrical derivatives of 2,2'-diquinoxalyl. In contrast to 6,6'-diquinoxalyls, which are readily obtained from 3,3'-diaminobenzidine, 2,2'-diquinoxalyls are much harder to obtain. The most common method for the preparation of symmetrical 3,3'-disubstituted 2,2'-diquinoxalyls is the condensation of vicinal tetraketones with o-phenylenediamine [2]. Symmetrical diquinoxalyls were also obtained by the catalytic dehydrogenation of quinoxaline derivatives [3], but the structures of the reaction products were not rigorously proved. As far as unsymmetrical 2,2'-diquinoxalyl derivatives are concerned, the literature contains only information on 3-amino- [4] and 3-phenyl-2,2'-diquinoxalyl [5] derivatives.

In the present research, to obtain unsymmetrical diquinoxalyls we used 2-acetylquinoxaline derivatives, which give 2-quinoxalylglyoxal monooximes (IIa-d) on nitrosation. The latter were converted to 3-R-7-R'-2,2'-diquinoxalyls (IIIa-d) by reaction with o-phenylenediamine.



I, II, III a R=C$_6$H$_5$, R'=H; b R=CH$_3$, R'=H; c R=R'=CH$_3$; d R=CH$_3$, R'=NHCOCH$_3$

We obtained the starting Ic,d previously in [1], while Ia,b were synthesized by the method in [6,7]; the reaction of 1-phenylbutane-1,2,3-trione with o-phenylenediamine gives a mixture of two isomers – 3-phenyl-2-acetylquinoxaline (Ia) and 3-benzoyl-2-methylquinoxaline (IV) – while only Ia was isolated in the studies indicated above.

The isomers were separated by chromatography. Bands at 1670 and 1716 cm^{-1}, which correspond to the vibrations of the carbonyl groups of the benzoyl and acetyl substituents, respectively, were observed in their IR spectra. According to the PMR spectrum, the product formed in the reaction consists of a mixture of Ia and IV (2 : 3). The chemical shifts for the methyl protons are 2.71 ppm for Ia and 2.66 ppm for IV (according to [8], the signals at 2.69 and 2.77 ppm were erroneously assigned to the acetyl protons of Ia and the methyl protons of IV, respectively).

EXPERIMENTAL

3-Phenyl-2-acetylquinoxaline (Ia) and 3-Benzoyl-2-methylquinoxaline (IV). The condensation of 1-phenylbutane-1,2,3-trione was carried out as described in [6,7] to give 47% of a product with mp 98-99° (mp 99.5° [8]). Two separations with a column filled with silica gel (elution with methylene chloride) gave

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*See [1] for communication I.

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a substance with mp 110-111° (from alcohol), which, according to above-indicated IR spectral data, the PMR spectrum, and the results of nitrosation, was 3-phenyl-2-acetylquinoxaline (Ia) (mp 111-113° [8]). The yield was 18%. Evaporation of the filtrate after separation of the mixture of Ia and IV gave 28% IV with mp 88-89° (from alcohol) (mp 89-91° [8]).

3-Methyl-2-(ω-isonitrosoacetyl)quinoxaline (IIb). A mixture of 0.46 g (2.5 mmole) of 2-methyl-3-acetylquinoxaline (Ib) and 0.3 g (2.6 mmole) of amyl nitrite in 5 ml of absolute alcohol was added gradually with ice cooling to a solution of sodium ethoxide, obtained from 0.07 g (0.003 g-atom) of sodium and 1 ml of absolute alcohol. The suspension was allowed to stand in a sealed flask for 12 h at 5-10° and was then poured into 8 ml of water. The unchanged Ib was separated, and the filtrate was washed with ether and acidified with 35% acetic acid to give 0.13 g (24%) of IIb with mp 176-177° (from aqueous alcohol). Found: C 61.2; H 4.2; N 19.5%. $C_{11}H_9N_3O_2$. Calculated: C 61.39; H 4.2; N 19.5%. UV spectrum, λ_{max}, nm (log ε): 240 (4.373), 315 (3.870). Evaporation of the ether solution gave 0.32 g of starting Ib.

3-Phenyl-2-(ω-isonitrosoacetyl)quinoxaline (IIa). This compound was obtained by the method used to prepare IIb from 0.785 g (3.2 mole) of Ia and 0.36 g (3.1 mole) of amyl nitrite in a solution of sodium ethoxide, obtained from 0.085 g of sodium in 6 ml of alcohol. The yield of product with mp 181-182° (from aqueous alcohol) was 0.22 g (25%). Found: C 69.1; H 4.0; N 14.9%. $C_6H_{11}N_3O_2$. Calculated: C 69.3; H 4.0; N 15.2%. UV spectrum, λ_{max}, nm (log ε): 245 (4.462), 330 (3.863).

3,7-Dimethyl-2-(ω-isonitrosoacetyl)quinoxaline (IIc). This compound was similarly obtained in 32% yield and had mp 195-196° (from alcohol). Found: C 62.9; H 4.9; N 18.2%. $C_{12}H_{11}N_3O_2$. Calculated: C 62.9; H 4.8; N 18.2%. UV spectrum, λ_{max}, nm (log ε): 245 (4.431), 325 (4.057).

3-Methyl-7-(N-acetamido)-2-(ω-isonitrosoacetyl)quinoxaline (IId). This compound was similarly obtained in 21% yield and had mp 203-204° (from aqueous alcohol). Found: C 54.2; H 5.0; N 18.9%. $C_{13}H_{12}N_4O_3 \cdot H_2O$. Calculated: C 53.8; H 4.9; N 19.3%.

3-Phenyl-2,2'-diquinoxalyl (IIIa). A 0.18-g (6.5 mmole) sample of IIa and 0.08 g (7.5 mmole) of o-phenylenediamine were refluxed for 10 h in 10 ml of ethylene glycol with 0.2 ml of acetic acid. The solution was cooled and poured into 10 ml of water, and the precipitate was washed with 5% hydrochloric acid. The yield of light-yellow product with mp 133-134° (from petroleum ether) was 0.156 g (72%). Found: C 78.9; H 4.0; N 16.6%. $C_{22}H_{14}N_4$. Calculated: C 79.0; H 4.2; N 16.8%. UV spectrum, λ_{max}, nm (log ε): 260 (4.568), 340 (4.243).

3-Methyl-2,2'-diquinoxalyl (IIIb). A 0.4-g (2 mmole) sample of IIb and 0.2 g (2 mmole) of o-phenylenediamine were dissolved by heating in 10 ml of alcohol, and the solution was refluxed for 2 h and cooled. The precipitate was removed by filtration to give 0.25 g (43%) of a product with mp 173-174° (from alcohol). Found: C 75.3; H 4.6; N 20.3%. $C_{17}H_{12}N_4$. Calculated: C 75.0; H 4.4; N 20.6%. UV spectrum, λ_{max}, nm (log ε): 260 (4.558), 335 (4.369).

3,7-Dimethyl-2,2'-diquinoxalyl (IIIc). This compound was obtained in 61% yield by the method used to prepare IIIb and had mp 181-182° (from alcohol). Found: C 75.7; H 5.1; N 19.3%. $C_{18}H_{14}N_4$. Calculated: C 75.5; H 4.9; N 19.6%.

3-Methyl-7-(N-acetamido)-2,2'-diquinoxalyl (IIId). This compound was similarly obtained in 48% yield and had mp 268-269° (from alcohol). Found: C 65.4; H 5.1; N 20.1%. $C_{19}H_{15}N_5O$. Calculated: C 65.7; H 4.9; N 20.2%.

The UV spectra (in alcohol) were recorded with an SF-4 spectrophotometer. The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrophotometer. The PMR spectra of CCl_4 solutions of the compounds were recorded with a JNM-3H-60 spectrometer.

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