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STRUCTURE OF 3-(o-HYDROXYPHENYL) DERIVATIVES OF 2-QUINOXALONE AND 2-BENZOXAZINONE

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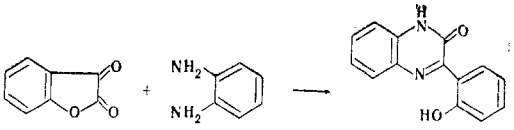
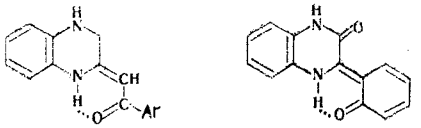
It is shown by IR and UV spectroscopy that the products of the reaction of o-hydroxybenzoylformic acid with o-phenylenediamine and o-aminophenol have the 3-(cyclohexa-3,5-dien-2-onylidene)quinoxalone structure rather than the 3-(o-hydroxyphenyl)-2-quinoxalone structure. 3-(o-Methoxyphenyl)-2-quinoxalone and 3-(o-methoxyphenyl)-3,4-dihydro-2H-benzo-1,4-oxazin-2-one were synthesized as model compounds.

In 1909, Fries [1], in an attempt to obtain coumarophenazine, carried out the condensation of coumarin-2,3-dione with o-phenylenediamine. However, the reaction product did not contain a furan ring. Fries proposed the 3-(o-hydroxyphenyl)-2-quinoxalone structure for the product.



The same compound can be obtained by reaction of o-hydroxybenzoylformic acid with o-phenylenediamine. The IR spectra of the Fries compound were investigated in 1973 [2]. It was observed that the spectrum does not contain the absorption characteristic for the stretching vibrations of the OH group. Banerji and coworkers [2] explained this by the fact that the OH line is masked by moisture in the KBr used to prepare pellets of the compound for recording of the spectra.

During a study of the products of the reaction of aroylpyruvic acids with o-phenylenediamine by PMR spectroscopy it was established that these compounds have the 3-phenacylidene-2-quinoxalone structure (I), in which there is an intramolecular hydrogen bond between the hydrogen of the NH group of the quinoxaline ring and the oxygen of the carbonyl function of the phenacylidene group.



I II

Considering the tendency of the quinoxaoline ring to form an exo ethylene bond, we assumed that the Fries compound has structure II. To prove the structure of II we investigated the IR and UV spectra of this compound, as well as the spectra of the products of the reaction of o-phenylenediamine (III) with benzoylformic (IV) and o-methoxybenzoylformic (V) acid esters.

The long-wave absorption maximum of II is found at 387 nm in the UV spectra (Fig. 1), whereas the corresponding maximum in the spectra of 3-phenyl-2-quinoxaolone (VI) and 3-(o-methoxy)phenyl-2-quinoxalone

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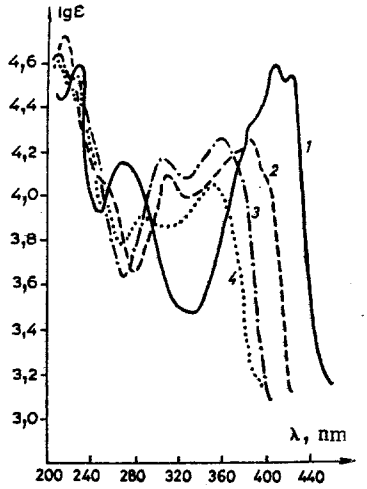


Fig. 1

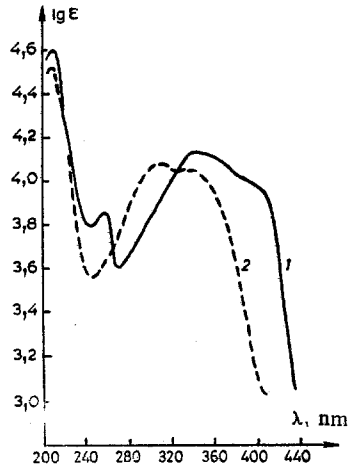


Fig. 2

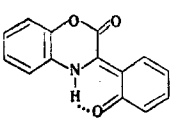
Fig. 1. UV spectra: 1) 3-phenacyl-2-quinoxalone; 2) 3-(cyclohexa-3,5-dien-2-onylidene)-2-quinoxalone; 3) 3-phenyl-2-quinoxalone; 4) 3-(o-methoxyphenyl)-2-quinoxalone.

Fig. 2. UV spectra: 1) 3-(cyclohexa-3,5-dien-2-onylidene)-3,4-dihydro-2H-benzo-1,4-oxazin-2-one; 2) 3-(o-methoxyphenyl)-3,4-dihydro-2H-benzo-1,4-oxazin-2-one.

(VII), for which the existence of a form with an exo bond is impossible, is found at 362 and 350 nm. This substantial shift in the long-wave maximum on passing from II to 3-(o-methoxyphenyl)-2-quinoxalone (VII) is impossible to explain if it is assumed that the two products have identically constructed heterocyclic rings. At the same time, the similarity in the spectral curves of I and II is explained by the fact that transmission of the electronic effects occurs via similar chains. The effect of the aryl group of the side chain in I leads to a certain bathochromic shift of the long-wave absorption maximum. Thus the UV spectra of the product of the reaction of o-hydroxybenzoylformic acid (VIII) and III correspond to structure II rather than to the 3-(o-hydroxyphenyl)-2-quinoxalone structure. The addition of from 1 to 20 equivalents of sodium ethoxide to an alcohol solution of II does not lead to a change in the character of the UV spectrum. Consequently, II is not converted to the o-hydroxy form under the investigated conditions. Evidence for the stability of the form with an exo ethylene bond is also provided by the inability of II to undergo cyclization to give the corresponding benzofuroquinoxalines; the corresponding 3-phenacylidene-2-quinoxalones readily form 2-arylfuroquinoxalines.

The IR spectrum also corresponds to structure II. As we have already mentioned above, the spectrum does not contain the absorption of a hydroxyl group but does contain bands at 1667 cm^{-1} (stretching vibrations of an amide carbonyl group), 1600 cm^{-1} (aromatic absorption), and 1573 cm^{-1}. The latter band corresponds to the vibrations of the carbonyl group of the cycloalkylidene ring in the 2 position. This frequency does not correspond to the absorption of the carbonyl group in o-quinones. Since II is the vinylog of an amide, this carbonyl group more likely has the character of an amide carbonyl group rather than the character of the carbonyl group in quinones. These compounds absorb at considerably lower frequencies than the corresponding o-quinones. Thus the carbonyl group in 1,4-dihydro-4-pyridone absorbs at 1548 cm^{-1} [3].

The IR and UV spectra of the products of the reaction of o-aminophenol (IX) with o-hydroxybenzoylformic acid (VIII) similarly confirm that this compound has structure X.



X

The UV spectra of the products of the reaction of o-aminophenol with o-hydroxybenzoyl- and o-methoxybenzoylformic acids are presented in Fig. 2. As in the case of quinoxalone derivatives, a hypsochromic shift (35 nm) of the long-wave absorption maximum is observed on passing from the spectrum of X to the spectrum of the corresponding 3-(o-methoxyphenyl)-3,4-dihydro-2H-benzo-1,4-oxazin-2-one (XI). In this case conver-

sion to the o-hydroxy form does not occur when 1 to 20 equivalents of sodium ethoxide are added to an alcohol solution of X.

EXPERIMENTAL

The UV spectra of $2.5 \cdot 10^{-5}$ M ethanol solutions of the compounds were recorded with a Specord UV-Vis spectrophotometer. The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-10 spectrometer.

3-(Cyclohexa-3,5-dien-2-onylidene)-2-quinoxalone (II). A total of 10 ml of an alcohol solution of 0.54 g (5 mmole) of III was added to a solution of 0.83 g (5 mmole) of VIII in 7 ml of alcohol, and the resulting yellow precipitate was removed by filtration to give 0.83 g (70.4%) of a product with mp 305-306°C (from acetic acid) [2].

Ethyl o-Methoxybenzoylformate (V). An ether solution of o-methoxyphenylmagnesium bromide, obtained from 3.4 g of magnesium and 18.7 g of o-bromoanisole, was added dropwise with stirring to 15 g of diethyl oxalate in 30 ml of absolute ether. At the end of the addition, the mixture was stirred at room temperature for 1 h, after which it was decomposed with 20% hydrochloric acid. The ether layer was washed successively with water, sodium bicarbonate, and water and dried with $MgSO_4$. The ether was removed by distillation, and the residue was vacuum fractionated with collection of the fraction with bp 183°C (15 mm) [4]. Found: C 63.8; H 5.8%. Calculated: C 63.5; H 5.8%.

3-(o-Methoxyphenyl)-2-quinoxalone (VII). A solution of 1.04 g (5 mmole) of V and 0.54 g (5 mmole) of III in 25 ml of mesitylene was refluxed for 1 h, after which it was cooled and worked up to give 0.6 g (47.6%) of product with mp 236-237°C (from alcohol). Found: C 69.2; H 4.7; N 11.1%. Calculated: C 69.0; H 4.8; N 11.1%.

3-(Cyclohexa-3,5-dien-2-onylidene)-3,4-dihydro-2H-benzo-1,4-oxazin-2-one (X). A mixture of 0.83 g (5 mmole) of VIII and 0.54 g (5 mmole) of IX in 20 ml of mesitylene was refluxed for 2 h, after which the solvent was removed to give 0.8 g (71.4%) of a product with mp 195-196°C (from alcohol). Found: C 70.4; H 3.7; N 6.2%. Calculated: C 70.3; H 3.8; N 5.9%.

3-(o-Methoxyphenyl)-3,4-dihydro-2H-benzo-1,4-oxazin-2-one (XI). Mesitylene (25 ml) was added to 1.04 g (5 mmole) of V and 0.54 g (5 mmole) of IX, and the mixture was refluxed for 2 h. It was then cooled and worked up to give 0.5 g (42.4%) of a product with mp 142-143°C (from alcohol). Found: C 71.3; H 4.3; N 5.8%. Calculated: C 71.1; H 4.4; N 5.5%.

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