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BENZOID-QUINOID TAUTOMERISM IN AZOMETHINES AND THEIR STRUCTURAL ANALOGS. 46.* SYNTHESIS AND REACTIONS OF 2-(N-ISATINOMETHYLENE)-3(2H)-BENZO[b]THIOPHENONE

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UDC 547.756'735:541. 623:535.37:543.422

Electronic, IR and UV spectroscopy has shown that 2-(N-isatinomethylene)-3(2H)-benzo[b]thiophenone in solution displays photo- and solvatochromism as a result of reversible E → Z isomerization, and it readily undergoes alcoholysis of the lactam bond. The resulting aminovinyl ketones exist as mixtures of the thermodynamically stable E- and Z-isomers.

We have previously shown that N-acylated 2-(N-arylaminomethylene)-3(2AH)-benzo[b]thiophenenones on irradiation with light undergo N → O acyl rearrangement as a result of photochemical Z → E isomerization [2].

The purpose of the present investigation was to synthesize an aminovinyl ketone with an N-acyl group, fixed by an additional bond in the o-position of the N-aryl ring, and to examine its structure, solvato- and photochromism, and in particular the possibility of occurrence of the above-mentioned reaction [2].

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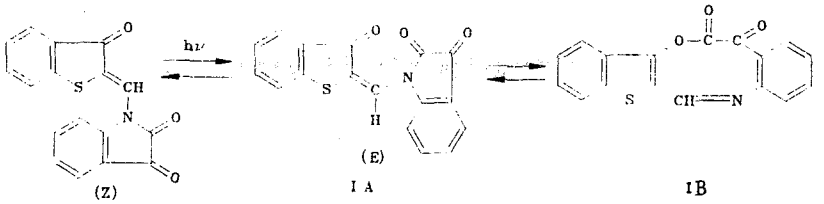
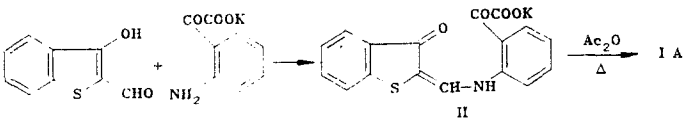
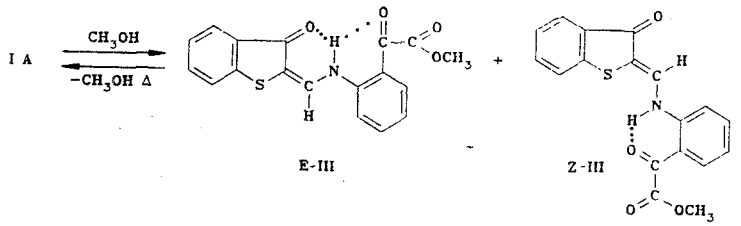


The subject chosen for study was the system (IA), the isatin fragment in which corresponds to an N-aryl-N-acyl grouping, with enhanced electrophilicity as a result of the influence of the α-dicarbonyl moiety. The compound (IA) was obtained from 3-hydroxybenzo[b]thiophene-2-carbaldehyde and potassium isatinate, obtained from isatin [3], to give the intermediate azomethine (II), which was then further cyclized by treatment with acetic anhydride to give (IA).



The electronic absorption spectra of (IA) show weak solvatochromism on changing from low to highly polar aprotic solvents (toluene–DMSO) (Fig. 1). Irradiation of solutions of (IA) with the total light output of a DRSh-250 lamp, or with sunlight, resulted in similar changes in the spectra, the intensity of the absorption at 460 nm increasing slightly, while the intensity of the bands with λ_{max} 312 and 424 nm decreased. The effect was reversible, in accordance with Z-(IA) ⇄ E-(IA) isomerization of (IA) at the C=C double bond, by analogy with other N-aryl-N-acylated heterocyclic aminovinyl ketones [2, 4]. The reaction (IA) ⇄ (IB) was not seen.

Compound (IA) reacts with alcohols, the electronic absorption spectra of alcoholic solutions of (IA) undergoing irreversible changes (Fig. 1). The rate of reaction is very rapid in methanol, decreasing in the sequence: methanol > ethanol > 2-propanol. The electronic spectra of the products of reaction of (IA) with alcohols were identical to that of the potassium salt of the aminovinyl ketone (II) (Fig. 1), suggesting the formation of the corresponding alkyl esters of the ketoacids by alcoholysis of the lactam ring. In fact, following solution of (IA) in methanol, orange-colored needles separated which, according to their elemental analysis and spectral characteristics, corresponded to the structure (III) (see Experimental).



The PMR spectrum of (III) indicated the presence in solution of two stable forms, probably the E- and Z-isomers. In solution in deuterochloroform, (III) showed a double set of signals for the NH protons (11.0 and 13.65 ppm, J = 14 Hz, indicating the predominance of the s-trans-aminovinyl ketone structure), one of the two doublets for the CH signals (8.40 ppm, J = 14 Hz, the second being masked by the signals for the aromatic protons), and two singlets for the methoxy protons (4.00 and 3.97 ppm).

The interconversion of the isomers E-(III) ⇄ Z-(III) has a high activation barrier. Reactions on the PMR time scale were not seen, even when catalyzed by trifluoroacetic acid, the doublet signals for CH (8.40 ppm) and NH (11.00 ppm) changing little on addition of the catalyst to the solution, and the coupling constant remained at 14 Hz. Heating an o-dichlorobenzene solution of the mixed isomers E-(III) and Z-(III) to 120°C likewise failed to result in coalescence of the signals for the methyl protons, indicating high free energy of activation

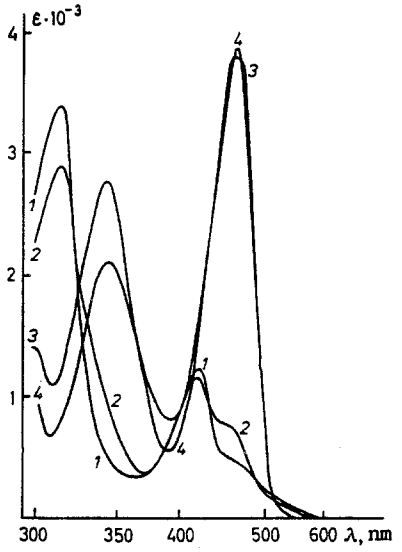
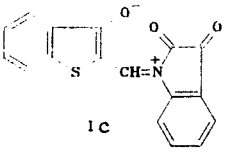


Fig. 1. Electronic absorption spectra: 1) (IA) in toluene; 2) (IA) in DMSO or after irradiation of the solution for three minutes with light from a DRSh-250 lamp; 3) (I) or (III) in methanol; 4) potassium salt (II) in methanol.

of the interconversion of the isomers (greater than 100 kJ/mole), which are stabilized by strong intramolecular hydrogen bonding. Prolonged heating of solutions of (III) at temperatures in excess of 100°C resulted in a decrease in the intensity of the methyl signals, with the appearance of a quantitatively equivalent signal for methanol protons, indicating that under these conditions the reverse cyclization of the isatin ring to give (IA) occurs. This reaction is most clearly seen on heating the crystalline aminovinyl ketone (III) under the microscope. At 168-169°C, the crystals of (III) melt to give a homogeneous liquid. On raising the temperature to 200-205°C, the melt is rapidly converted into crystals of (IA) with loss of methanol, these crystals finally melting at 269-270°C.

This unusually facile alcoholysis of the lactam bond in the isatin ring induces cleavage under the influence of the 2-methylidene-3(2H)-benzo[b]thiophene residue, which causes polarization of the conjugated system as a result of a large contribution by the resonance form (IC) [5]. N-Acylated and other isatin derivatives do not react with alcohols in this way [6].



Ic

EXPERIMENTAL

IR spectra were obtained on a Specord IR-71 in vaseline grease, and electronic absorption spectra on an M-40 instrument. PMR spectra were recorded on a Tesla BS-567A (100 MHz) in chloroform, DMSO-D_6, or o-dichlorobenzene, partially in Fourier mode, internal standard HMDS.

The elemental analyses of (I)-(III) for C, H, and N were in agreement with the calculated values.

3-Hydroxybenzo[b]thiopene-2-carbaldehyde was obtained as described in [7], by formylation of thianaphthene.

Potassium Salt of 2-(N-o-Oxalophenylaminomethylene)-3(2H)-benzo[b]thiophenone (II, $C_{17}H_{10}KNO_4S$). To a solution of 1 g (5 mmole) of potassium isatinate [3] in 10 ml of methanol was added 0.9 g (5 mmole) of 3-hydroxybenzo[b]thiophene-2-carbaldehyde. The solution was heated for 20 min on the water bath at 50°C, cooled, and the yellow precipitate of the salt (II) filtered off and recrystallized from methanol, mp 220°C. IR spectrum: 1660, 1630 (CO), 3400 cm^{-1} (NH). UV spectrum (methanol), λ_{max} ($\varepsilon \cdot 10^{-3}$); 340 (2.81), 463 nm (3.86).

2-(N-Isatinomethylene)-3(2H)-benzo[b]thiophenone (I, $C_{17}H_9NO_3S$). The potassium salt (II) 0.4 g, 1 mmole) was dissolved with heating in 20 ml of acetic anhydride, and the solution boiled for three minutes, and cooled. The solid (I) which separated was filtered off and washed with chloroform, mp 269-270°C (from acetic anhydride). Yield 0.28 g (95%). IR spectrum: 1740, 1670 cm^{-1} (CO). PMR spectrum (DMSO-D_6): 7.35-7.86 (Ar), 7.95 ppm (CH).

2-(N-o-Methoxalylphenylaminomethylene)-3(2H)-benzo[b]thiophenone (III, $C_{15}H_{13}NO_4S$). Compound (I) (0.2 g, 5 mmole) was dissolved with heating in 10 ml of methanol, and the solution boiled for 15 min. On cooling, orange-colored crystals of (III) separated, mp 168-169°C. Yield 0.1 g (45%). IR spectrum: 1730, 1670, 1650 (CO), 1200 (CO), 3400 cm^{-1} (NH).

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DEPENDENCE OF THE REACTIVITY OF FIVE-MEMBERED AROMATIC HETEROCYCLES ON THEIR STRUCTURE.

4.* PROTON AFFINITY OF N-AMINOAZOLES

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Proton affinity of the amino groups of 10 N-aminoazoles is calculated using the STO-3G basis set. The nature of the heterocyclic effect on proton affinity of the amino groups depends on its conformation which in turn is determined by the number of nitrogen atoms in the α-position. The accuracy of the proton affinity calculation can be raised considerably by taking into account the interaction of heteroatoms in the ring.

We demonstrated that the proton affinity (PA) in the case of C-aminoazoles upon protonation at the amino group can be calculated by a simple additive scheme [2] by studying the dependence of PA of aminoazoles on the number and position of the heteroatoms. In the present case, we studied the possibility of using this scheme for description of the effect of heteroatoms on the PA of the amino group in a number of N-aminoazoles. The PA (Table 1) of all possible N-aminoazoles which also contain from 0 to 4 nitrogen atoms in the ring are estimated from the formula

$$PA = E^0 - E^+, \quad (1)$$

where E^0 and E^+ are the total energies of the starting and protonated azole which are calculated using the STO-3G minimal basis set according to the procedure described in [2].

Optimization of the geometry of the $N\text{-}NH_2$ fragment within the framework of the semiempirical MNDO method shows that the tetrahedral amino group in N-aminoazoles with one α-nitrogen

*For Communication 3, see [1].

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