SYNTHESIS AND SPECTROSCOPIC STUDY OF ARYLAZO DERIVATIVES OF BENZIMIDAZOLO[2',1':2,3]THIAZOLIDIN-4-ONE

I. I. Chizhevskaya, M. I. Zavadskaya, and N. N. Khovratovich

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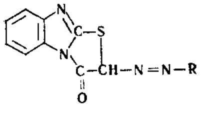
The coupling of benzimidazolo[2', 1':2, 3]thiazolidin-4-one with benzenediazonium chlorides in acetic acid in the presence of sodium acetate at pH 4.5-4.0 has yielded 5-arylazo derivatives of the thiazolidone. By a study of the IR and UV spectra of the aryl derivatives of benzimidazolo[2', 1':2, 3]thiazolidin-4-one synthesized, it has been shown that the latter has the azo structure.

It is known that the hydrogen atoms of the methylene group of benzimidazolo[2',1':2,3]thiazolidin-4-one (I) possess a high mobility, which is shown by the capacity of I for reacting with aldehydes, ketones, nitroso compounds, and diazonium salts to form 5-benzylidene, azomethine, and azo derivatives of the thiazolidin-4-one [1, 2].

The object of the present work was to study the reaction of I with the diazonium chlorides obtained from aniline and p-nitro-, p-sulfamoyl-, p-carboxy-, and p-sulfoanilines, and also to study the structure of the phenylazo derivatives of I obtained by IR and UV spectroscopy. The experiments on the coupling of I with the above-mentioned benzenediazonium salts in an alkaline medium gave negative results in view of the instability of the thiazolidone ring in I to the action of alkaline agents. When I was coupled in aqueous solutions of caustic soda (2–5%), 2-benzimidazolylthioacetic acid, contaminated with the products of decomposition of the diazonium compound, was isolated from the reaction mixture.

Coupling of I with benzenediazonium salts in glacial acetic acid in the presence of anhydrous sodium acetate at a pH of 4.5–5.0 gave the 5-phenylazo derivatives of I with a yield of about 70% (compounds II–VI). The properties of the azo compounds obtained are given in the table.



II R=C_6H_5
III R=p-NO_2—C_6H_4
IV R=p-H_2N—SO_2—C_6H_4
V R=p-HOOC—C_6H_4
VI R=p-HO_3S—C_6H_4

Azo derivatives II–VI synthesized consist of yellow or orange-yellow microcrystalline powders readily soluble in aqueous solutions of alkalies with the formation of a crimson-red color. When the alkaline solutions were acidified, the azo compounds were precipitated unchanged. The azo derivatives II, IV, V, and VI were not reduced at the N=N bond by sodium hydrosulfite either in ethanol or in alkaline medium. Negative results were obtained in experiments on the reduction of II and VI with Raney nickel in ethanol at temperatures of 30 and 70° C. Reduction of II, V, and VI with zinc dust in an aqueous ammoniacal medium apparently stopped at the stage of the formation of the hydrazo compound, which can explain the partial decoloration of the dye solutions observed in the experiments and the appearance of the original coloration when the solutions were allowed to stand in the air.

In order to study the structure of the azo compounds synthesized, their IR and UV spectra were investigated. From a consideration of the IR spectra of compounds II–IV and a comparison of them with the IR spectrum of the initial I (Fig. 1), it follows that in the region of the stretching vibrations of the double bonds a clear absorption band appeared in the spectra of the azo compounds in the 1550–1575 cm^{-1} region which was absent from the IR spectrum of I. This band does not overlap the band of the stretching vibrations of the C=N bond and the bands appearing in the 1550–1575 cm^{-1} region in the IR spectra of II–IV to be assigned to the stretching vibration of the N=N bond [3,4].

Absence from the IR spectra of absorption bands associated with the stretching vibrations of the imino

5-Arylazo Derivatives of Benzimidazolo[2',1':2,3]thiazolidin-4-one

Compound	Aryl	Mp, °C (solvent)	Empirical formula	Found, %			Calculated, %			Yield, %
				C	H	N	C	H	N	
II	Phenyl	255.5—256.0 (ethanol)	$C_{15}H_{10}N_4OS$	60.84 61.08	3.78 3.46	18.76 18.68	61.23	3.41	19.05	70.0
III	p-Nitrophenyl	283.0—284.0 (n-propanol)	$C_{15}H_9N_5O_3S$	52.81 52.94	3.07 2.91	20.21 20.40	53.09	2.65	20.65	73.0
IV	p-Sulfamoylphenyl	242.0—245.0 (ethanol)	$C_{15}H_{11}N_5O_3S_2$	48.01 47.96	2.61 2.58	18.41 18.56	48.26	2.94	18.76	70.8
V	p-Carboxyphenyl	307.5—308.0 (ethanol)	$C_{16}H_{10}N_4O_3S$	56.98 57.03	3.17 3.21	16.27 16.41	12.38	2.95	16.55	72.0
VI	p-Sulfophenyl	above 330.0 (water)	$C_{15}H_{10}N_4O_4S_2 \cdot 4H_2O$	40.64 40.27	3.84 3.87	56.80 40.38	12.09	4.03	12.35	66.0

group =NH (3400–3300 cm^{-1}) permits the assumption that the compounds synthesized exist in the azo form.

The UV spectra of azo compounds II and III (Fig. 2) are characterized by the presence of absorption maxima at 382 and 400 nm, respectively, which are connected with the presence of an azo group in them. Bathochromic shift of the absorption maximum of the N=N group by 18 nm, observed in the UV spectrum of the 5-p-nitrophenylazo derivative III, is a confirmation of the existence of III in the azo form [5, 6].

EXPERIMENTAL

Synthesis of the arylazo derivatives of benzimidazolo[2',1':2,3]-thiazolidin-4-one (II–VI). The aryldiazonium chloride obtained by the diazotization of 0.01 mole of aniline or p-nitro, p-sulfamoyl-, p-carboxy-, or p-sulfoaniline with sodium nitrite [7] was added dropwise to 1.9 g (0.01 mole) of I dissolved in 50 ml of glacial acetic acid. Azo coupling took place at a temperature of 10–15° C in the presence of 3.8–4.0 g of anhydrous sodium acetate, which was added in portions during the reaction. The azo derivatives separated out in the form of yellow and yellow-orange microcrystalline precipitates when the reaction mixture was diluted with water. Characteristics of the arylazo derivatives obtained are given in the table.

Attempts to reduce the arylazo derivatives II, V, and VI. a) With sodium hydrosulfite. An aqueous solution of 0.01 mole of sodium hydrosulfite was added to a boiling solution of 0.002 mole of an azo compound in 50 ml of ethanol. Heating was continued for 1 hr 30 min. A mixture of the substance isolated from the reaction mixture and the initial azo compound gave no depression of the melting point. The same negative results were obtained in experiments on the reduction of II, and IV, and VI with sodium hydrosulfite in an alkaline medium (0.4–5.0% aqueous solutions of caustic soda and 5–10% solutions of sodium carbonate) at temperatures of 50 and 80° C.

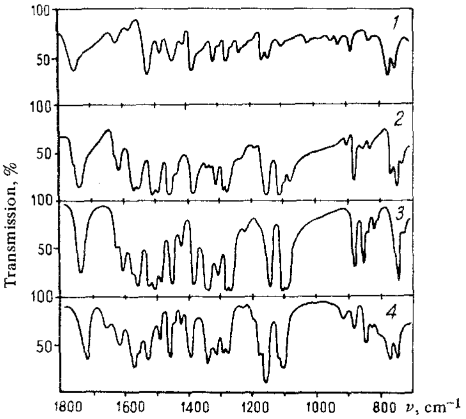


Fig. 1. IR spectra of: 1) benzimidazolo[2',1':2,3]thiazolidin-4-one (I); 2) 5-phenylazobenzimidazolo[2',1':2,3]thiazolidin-4-one (II); 3) 5-p-nitrophenylazobenzimidazolo[2',1':2,3]thiazolidin-4-one (III); 4) 5-p-sulfamoylphenylazobenzimidazolo[2',1':2,3]thiazolidin-4-one (IV).

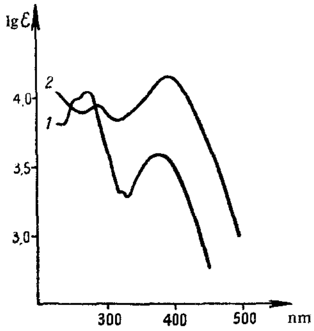


Fig. 2. UV spectra of: 1) 5-phenylazobenzimidazolo [2',1';2,3]thiazolidin-4-one (II); 2) 5-p-nitrophenylazobenzimidazolo [2',1':2,3] thiazolidin-4-one (III).

b) With zinc dust in an aqueous ammoniacal medium. In experiments on the reduction of the azo compounds with zinc dust in 5% ammonia solution at 50–60° C, a change in the original coloration of the solutions of the azo compounds from orange-red to yellow was observed. On standing in air, the original coloration of the solutions was restored, and when the alkaline solutions were acidified the initial azo compounds precipitated.

The IR spectra were recorded on a UR-10 infrared spectrometer using KBr, NaCl, and LiF prisms. The samples were investigated in compressed KBr tablets.

The UV spectra were measured on an SF-4 spectrophotometer in methanol at a concentration of the substances of 1 × 10^{-4} M.

REFERENCES

1. J. A. Van Allan, J. Org. Chem., 21, 24, 1956.

2. I. I. Chizhevskaya, L. I. Gapanovich, and L. V. Poznyak, ZhOKh, 33, 945, 1963.

3. F. A. Snavely, W. S. Trahanovsky, and F. H. Snydam, J. Org. Chem., 27, 994, 1962.

4. J. Jander and R. Haszeldine, J. Chem. Soc., 919, 1954.

5. A. Gillem and E. Stern, An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry [Russian translation], IL, p. 164, 1957.

6. A. A. Kharkharov, Izv. AN SSSR, OKhN, 326, 1071, 1955.

7. H. E. Fierz-David and L. Blangey, Fundamental Processes of Dye Chemistry, [Russian translation], IL, p. 225, 1957.

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Institute of Physical Organic
Chemistry AS Belorussian SSR,
Minsk