SYNTHESIS AND SPECTROSCOPIC INVESTIGATION OF SOME ARYLAZO DERIVATIVES OF THIAZOLIDIN-4-ONE

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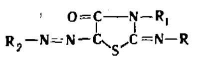
The reaction of 2-phenylimino- and 2-(p-tolylimino)thiazolidin-4-ones with benzene-, p-nitrobenzene, p-sulfamoylbenzene-, and p-toluenediazonium chlorides in glacial acetic acid in the presence of anhydrous sodium acetate (pH of the medium 4.5–5.0) has been studied. A spectroscopic investigation in the IR and UV regions has shown that the 5-(p-nitrophenylazo) derivatives of thiazolidin-4-one exist in the azo tautomeric form; the 5-phenylazo and p-tolylazo derivatives of thiazolidin-4-one are mixtures of the azo and hydrazone tautomers.

It is known from the literature [1] that derivatives of 2-iminothiazolidin-4-one are capable of reacting with diazonium salts through the mobile hydrogen atoms in the methylene group. Products of the coupling of 2-phenyliminothiazolidin-4-one (I) and 2-(p-tolylimino)thiazolidin-4-one (II) with diazonium salts in an alkaline medium have been described [2,3], and it has been shown that the azo derivatives of I and II are readily reduced to the corresponding 5-amino derivatives with sodium hydrosulfite in ethanol [4]. The structure of the coupling products obtained has not been studied. It is known that the coupling reaction of diazonium salts with various compounds containing active methylene groups can take place over wide pH ranges of the medium and, in particular, benzimidazo[2,1-b]thiazolidin-3-one readily reacts with benzenediazonium salts in glacial acetic acid in the presence of sodium acetate [5].

The object of the present work was to study the interaction of I and II with diazonium salts in an acid medium and to investigate by IR and UV spectroscopy the structure of the products obtained. We have shown that I and II take part in the azo coupling reaction with diazotized aniline, p-nitroaniline, p-sulfamoylaniline, and p-toluidine in glacial acetic acid in the presence of sodium acetate at a pH of the medium of 4.5–5. The properties of the 5-arylazo derivatives of I and II (III–X) are given in the table. The coupling of I and II with two equivalents of the diazonium salts in an acid medium gave azo compounds identical with those described above.


III-X

III $R=R_2=C_6H_5$; $R_1=H$
IV $R=C_6H_5$; $R_1=H$; $R_2=p\text{-}NO_2C_6H_4$
V $R=C_6H_5$; $R_1=H$; $R_2=p\text{-}CH_3C_6H_4$
VI $R=p\text{-}CH_3C_6H_4$; $R_1=H$; $R_2=p\text{-}NO_2C_6H_4$
VII $R=p\text{-}CH_3C_6H_4$; $R_1=H$; $R_2=C_6H_5$
VIII $R=CH_2C_6H_5$; $R_1=CH_2C_6H_5$; $R_2=p\text{-}NO_2C_6H_4$
IX $R=C_6H_5$; $R_1=H$; $R_2=p\text{-}H_2NSO_2C_6H_4$
X $R=p\text{-}CH_3C_6H_4$; $R_1=H$; $R_2=p\text{-}H_2NSO_2C_6H_4$

The phenylazo compounds synthesized differ from analogous compounds described in the literature [2,3] with respect to the color of the crystals; the melting points of III, VII, and IX did not correspond to the melting points for these compounds in the literature: they were higher than the latter by 117, 88, and 205° C, respectively. Compounds III–VIII were reduced at the N=N bond with sodium hydrosulfide neither in ethanol nor in aqueous solutions of caustic soda, ammonia, and sodium carbonate.

To study the structure of the phenylazo derivatives synthesized, compounds III–VIII were subjected to a spectroscopic investigation in the IR and UV regions.

It follows from a consideration of the IR spectra of III–VIII (Fig. 1) that in the region of vibrations of double bonds, a band with a frequency of 1555 cm^{-1} appeared in the spectrum of III which was absent from the spectrum of the initial I. A similar band in the 1550–1575 cm^{-1} range is found in the IR spectra of the other azo compounds studied IV–VIII. The band mentioned does not overlap the band of the stretching vibrations of the C=N bond and the bands due to the vibrations of the aromatic ring. All the above facts permit the band in the 1550–1575 cm^{-1} region to be ascribed to the stretching vibrations of the N=N bond. The IR spectra of III, V, and VII have bands with frequencies of 3385, 3380, and 3375 cm^{-1}, respectively, while in the spectrum of V the 3380 cm^{-1} band is particularly strong. There are no absorption bands in this region in the IR spectra of IV and VI. In the spectrum of VIII, in the region of vibrations of the NH bond, both the absorption band with the frequency of 3375 cm^{-1} and the band with a frequency of 3265 cm^{-1} due to the stretching vibrations of the ring NH bond are absent. The spectral data discussed permit the conclusion that III, V, and VII exist in the form of a mixture of azo and hydrazone tautomers with an overwhelming predominance of the azo form, while IV, VI, and VIII have the azo structure.

The results of the studies in the IR region are confirmed by investigations in the UV region. It follows from a consideration of the UV spectra of III, IV, V, and VII (Fig. 2) that the bands with absorption maxima at 376, 418, 396, and 394 nm are due to the presence of the N=N group in the compounds studied. The displacement of the absorption maximum of the N=N group to the long-wave part of the spectrum by 42 nm in the spectrum of IV caused by the presence of a nitro group in the chain of conjugated double bonds with the azo group is a confirmation of the existence of IV in the azo form [6,7,8]. The absorption maxima at 236 and 239 nm observed in the UV spectra of III, V, and VII and absent from the spectra both of the initial I, which has one absorption maximum at 264 nm, and of IV, are apparently connected with the presence of the hydrazone tautomeric form in III, V, and VII.

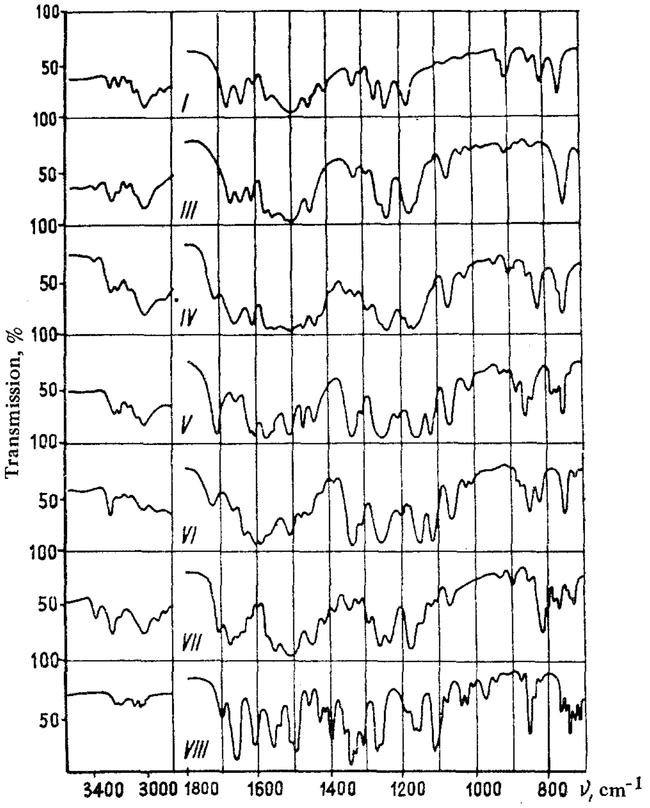


Fig. 1. IR spectra of the 5-arylazo derivatives of thiazolidin-4-one: I) 2-phenyliminothiazolidin-4-one; III) 5-phenylazo-2-phenyliminothiazolidin-4-one; IV) 5-(p-nitrophenylazo)-2-phenyliminothiazolidin-4-one; V) 5-(p-tolylazo)-2-phenyliminothiazolidin-4-one; VI) 5-(p-nitrophenylazo)-2-(p-tolylimino)thiazolidin-4-one; VII) 5-phenylazo-2-(p-tolylimino)thiazolidin-4-one; VIII) 5-(p-nitrophenylazo)-3-benzyl-2-benzyliminothiazolidin-4-one.

The existence of the 5-azo derivatives of I and II in one form or the other probably depends on the nature of the substituent entering into conjugation with the azo group. The presence of the electron-accepting nitro group in the para position of the benzene ring with respect to the azo group in IV, VI, and VIII causes a displacement of the tautomeric equilibrium in the direction of the azo form, while a methyl group favors an increase in the content of the hydrazone form in the tautomeric mixture (IR spectrum of V).

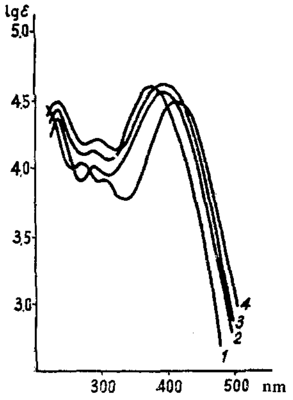


Fig. 2. UV spectra of 5-arylazo derivatives of thiazolidin-4-one: 1) 5-phenylazo-2-phenyliminothiazolidin-4-one (III); 2) 5-phenylazo-2-(p-tolylimino)thiazolidin-4-one (VII); 3) 5-(p-tolylazo)-2-phenyliminothiazolidin-4-one (V); 4) 5-(p-nitrophenylazo)-2-phenyliminothiazolidin-4-one (IV).

On the basis of data in the literature on the existence in the hydrazone form of products of the azo coupling of rhodanine with diazo compounds in an alkaline medium [9,10] an analogous structure may be assumed for the arylazo derivatives of I and II described in the literature [2,3]. In view of this, it appeared to us to be of interest to compare the IR and UV spectra of the azo derivatives of I and II synthesized in the present work with the spectra of the azo derivatives described in the literature. However, attempts to obtain azo compounds of I and II by coupling the latter with diazonium compounds in an alkaline medium, both under the conditions described in the literature and with modifications of them, were unsuccessful—the unchanged I or II, contaminated with resinous products of the decomposition of the diazonium compound in an alkaline medium, were recovered from the reaction mixtures.

EXPERIMENTAL

The IR spectra of the azo compounds III–XIII were recorded on a UR-10 infrared spectrophotometer using LiF, NaCl, and KBr prisms. The samples were studied in the form of tablets molded in KBr. The UV spectra of compounds I, III, IV, V, and VII were measured on an SF-4 spectrophotometer in methanol at a concentration of the substances of 1×10^{-4} mole/*l*.

3-Benzyl-2-benzylimino-5-(p-nitrophenylazo)thiazolidin-4-one (VIII). A solution of 0.69 g (0.005 mole) of p-nitroaniline in 2 ml of concentrated HCl diluted with 1 ml of water was diazotized with 0.4 g of sodium nitrite in 1 ml of water. The resulting p-nitrobenzenediazonium salt was added over 15 min at room temperature with vigorous stirring to a solution of 1.48 g (0.005 mole) of 3-benzyl-2-benzyliminothiazolidin-4-one in 50 ml of glacial acetic acid containing 4.0 g of anhydrous sodium acetate. The solution became orange yellow and deposited a microcrystalline precipitate. It was stirred for 6 hr and then the precipitate was filtered off and recrystallized from methanol and then from acetone. Orange-yellow crystalline powder with mp 204° C (52%). Found, %: C 61.64; H 4.24. Calculated for $C_{23}H_{19}N_5O_3S$, %: C 62.02; H 4.26.

5-Phenylazo-2-phenyliminothiazolidin-4-one (III). A solution, prepared with heating, of 0.93 g (0.01 mole) of aniline in 3 ml of concentrated HCl diluted with 3 ml of water, was diazotized with 0.72 g of sodium nitrite in 3 ml of water. The solution of benzenediazonium salt was added over 30 min to a solution of 1.9 g (0.01 mole) of I in 60 ml of glacial acetic acid containing 2.0 g of anhydrous sodium acetate (pH 4.5–5.0) with vigorous stirring and cooling to 0–5° C. The homogeneous golden yellow solution obtained was kept in the refrigerator for 18 hr and was then poured into 200–300 ml of water. The III was filtered off and repeatedly washed on the filter with hot water. It was purified by three reprecipitations from solutions in 2% sodium hydroxide with acetic acid and subsequent recrystallization from acetic acid.

5-Arylazo Derivatives of 2-Aryliminothiazolidin-4-ones

Compound	Mp, °C	Empirical formula	Found, %			Calculated, %			Yield, %
			C	H	S	C	H	S	
III	250	$C_{15}H_{12}N_4OS \cdot H_2O$	57.64	4.67	10.36	57.35	4.45	10.19	32
IV	290	$C_{15}H_{11}N_5O_3S \cdot 1.5\ H_2O$	49.16	3.89	7.88	48.91	3.80	8.10	40
V	240	$C_{16}H_{14}N_4OS$	62.18	4.74	10.27	61.93	4.51	10.32	38
VI	289	$C_{16}H_{13}N_5O_3S \cdot 1.5\ H_2O$	50.40	3.94	8.43	50.26	4.18	8.37	40
VII	240	$C_{16}H_{14}N_4OS \cdot H_2O$	58.54	4.82	8.95	58.53	4.87	9.75	31
IX	290	$C_{15}H_{13}N_5O_3S_2 \cdot H_2O$	45.60	3.82	16.14	45.08	3.81	16.28	36
X	288	$C_{16}H_{15}N_5O_3S_2 \cdot 1.5\ H_2O$	46.20	4.59	14.10	46.15	4.32	15.20	38

Compounds IV–X were obtained in a similar manner to III; they consisted of yellow or orange-yellow microcrystalline powders (from acetic acid) soluble in acetic acid, acetone, and ethanol. On dissolution in alkali, they have crimson-red or violet solutions.

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