3-ARYL-4,5-DICHLORO-1,2,3-THIADIAZOLIUM SALTS — SYNTHONS FOR THE PREPARATION OF MESOIONIC COMPOUNDS OF THE 1,2,3-THIADIAZOLE SERIES

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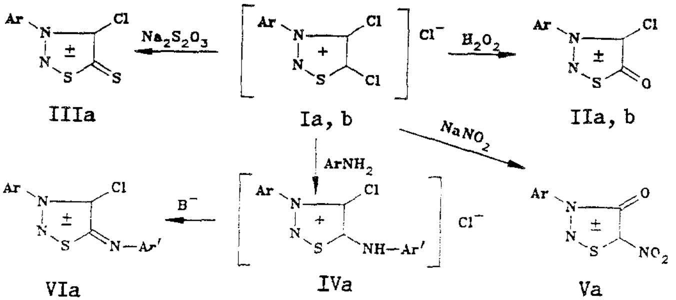
The high mobility of the chlorine atom at the 5-position of 3-aryl-4,5-dichloro-1,2,3-thiadiazolium salts facilitates a ready preparation of mesoionic 3-aryl-1,2,3-thiadiazoles with an exocyclic oxygen, sulfur or arylimino group at the 5-position. In an aqueous alcoholic solution of sodium nitrite, the halogens in the 4- and 5-positions are substituted with the formation of 3-aryl-5-nitro-1,2,3-thiadiazolium-4-olates.

3-Aryl-4,5-dichloro-1,2,3-thiadiazolium (I) chlorides were obtained by the reaction of N-nitroso-N-arylaspartic acids with thionyl chloride [1, 2]. The reaction proceeds through the intermediate of 3-aryl-4-carboxymethylsydnones, which can be isolated using a special technique [1]. The same chlorides of compound I can be obtained in a higher yield and degree of purity [2] by treatment of 3-aryl-4-carboxymethylsydnones.

The ready exchange of ionogenic chlorine in salts of I for other anions is taken advantage of for their purification by converting them into perchlorates. It was found that the chlorine atom at the 5-position is readily exchanged for oxygen, sulfur atoms, arylimino and nitro groups; thus new mesoionic compounds of the 1,2,3-thiadiazole series were obtained:



I–VI a Ar=C_6H_5; b Ar=p-$CH_3C_6H_4$

We have previously reported the synthesis of 3-aryl-4-chloro-1,2,3-thiadiazolium-4-olates II and 3-aryl-4-chloro-1,2,3-thiadiazolium-5-arylaminides VI via salts IV [3], by oxidizing the salts of I [2] and their reaction with arylamines in acetic acid, respectively.

A representative of a new mesoionic system — 3-phenyl-4-chloro-1,2,3-thiadiazolium-5-thiolate IIIa — was obtained by the action of thiourea in boiling acetic acid, sodium sulfide, potassium thiocyanate or sodium thiosulfate on salt Ia; the best yield was obtained with sodium thiosulfate.

In the reaction of Ia perchlorate or chloride in an aqueous-alcoholic medium with sodium nitrite, a "conjugated" substitution of chlorine atoms at the 4 and 5-positions was observed with the formation of derivatives 3-phenyl-5-nitro-1,2,3-thiazolium-4-olate Va. The only representative of this class was obtained [4] by nitration of 3-(p-tolyl)-1,2,3-thiadiazolium-4-olate unsubstituted at the 5-position. A compound having one chloride atom substituted at the 5-position by a nitro group could not be isolated, and this step is obviously the limiting one.

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In the UV spectra of the series 3-phenyl-4-chlorosydnone [5] → I → VIa → IIIa, a considerable bathochromic shift of the long wave absorption band is observed: 320 → 370 → 432 - 456 nm, while the short wave band undergoes a less appreciable shift (226 → 260 → 262 → 275 nm).

A sharp decrease of 100 nm on an average is observed in the IR spectra of the 1,2,3-thiadiazolium derivatives II-VI in the vibration frequencies of the exocyclic C=O and C=S groups, compared with the data for the sydnones. A somewhat lesser decrease in the vibration frequencies is observed in the case of the exocyclic C=N bond, compared with the decrease for acylsyndnonimines (by 40-60 nm), but this undoubtedly is due to the influence of the acyl group of sydnonimines.

These data, as well as the results of the x-ray diffraction investigations, published previously in [3, 6, 7] indicate a decrease in the double bond character of the exocyclic group in mesoionic derivatives of 1,2,3-thiadiazoles and an increase in their aromatic character in comparison with sydnones.

The mesoionic 1,2,3-thiadiazoles are stable to hydrolysis by dilute and concentrated acids because of their ready protonation. Our attempts to carry out the catalytic reduction of mesoionic 1,2,3-thiadiazolium-5-acylaminides were unsuccessful, as were the attempts at 1,3-dipolar cycloaddition with acetyldicarboxylate, characteristic for sydnones. Similar results were published by the Japanese authors in [8].

Thus, the mesoionic 3-aryl-1,2,3-thiadiazolium compounds with an exocyclic group at the 5-position most closely fit the modern concepts on the structure of mesoionic compounds [9, 10] and, in contrast to sydnones stabilized by 1,3-dipoles, comprise stable 6π-electronic heteroaromatic systems with a considerable negative charge localized on the exocyclic group, due to an additional unshared electron pair of the exocyclic atom.

EXPERIMENTAL

The PMR spectra were recorded in DMSO-D_6, on PH 2305 (60 MHz) and BS-487 (80 MHz) spectrometers, using HMDS as internal standard. The mass spectra were obtained on an MX-1303 mass spectrometer (50 eV, 120°C). The IR spectra were run on a UR-20 spectrophotometer (KBr tablets), and the UV spectra on SF-26 and Specord M40 spectrophotometers. The course of the reactions was monitored by TLC on Silufol UV-254 plates, using chloroform and a chloroform—methanol (10:1) mixture as eluents.

The data of the elemental analyses of compounds III-VI for C, H, N, S correspond to the calculated values.

3-Phenyl-4,5-dichloro-1,2,3-thiadiazolium (Ia) chloride was obtained according to [1, 2], yield 38%, mp 250°C (dec.) [1].

3-Phenyl-4-chloro-1,2,3-thiadiazolium-5-olate (IIa) was synthesized according to [3]. IR spectrum, ν, 1640 cm^{-1} (C=O). UV spectrum, λ_{max} (log τ): 230 (3.9), 260 (3.85), 370 nm 3.65).

3-Phenyl-4-chloro-5-phenylamino-1,2,3-thiadiazolium Chloride (IVa, $C_{14}H_{11}Cl_2N_3S$). A 0.9 g portion (0.01 mole) of aniline was added to a solution of 2.7 g (0.01 mole of 3-phenyl-4,5-dichloro-1,2,3-thiadiazolium chloride in 20 ml of acetic acid, and the mixture was heated at 115°C for 3 h. The precipitate that separated out on cooling was filtered off, and washed with cold acetic acid. Yield, 64%, mp 226-228°C (dec.).

3-Phenyl-4-chloro-1,2,3-thiadiazolium-5-phenylaminide (VIa). A 2.7 g portion (0.01 mole) of 3-phenyl-4-chloro-5-phenylamino-1,2,3-thiadiazolium chloride was dissolved with slight heating in 30 ml of 50% ethanol, and a small excess of 15% aqueous ammonia was added. The mixture was allowed to stand for 24 h, and the ruby-red crystals were filtered off and recrystallized from benzene. Yield, 83%, mp 123-124°C. IR spectrum: 1545 cm^{-1} (C=N). Mass spectrum: M^+ 287. UV spectrum λ_{max} (log ε): 262 (4.42), 432 nm (3.83).

3-Phenyl-4-chloro-1,2,3-thiadiazolium-5-thiolate (IIIa, $C_8H_5ClN_2S_2$). An aqueous solution of 5.0 g (0.02 mole) of sodium thiosulfate was added to a hot solution of 5.4 g (0.02 mole) of 3-phenyl-4,5-dichloro-1,2,3-thiadiazolium chloride in 50% ethanol. The orange precipitate was filtered off, and washed on the filter with water. On recrystallization from a benzene—petroleum ether (1:1) mixture, bright orange plates were obtained. Yield 84%, mp 250-251°C. IR spectrum (in KBr): 1380, 1260 cm^{-1} (C=S). Mass spectrum: M^+ 195.5. UV spectrum (in alcohol), λ_{max} (log ε): 275 (4.01), 456 nm (3.60).

3-Phenyl-5-nitro-1,2,3-thiadiazolium-4-olate (Va, $C_8H_5N_3O_3S$). A solution of 1 g (0.012 mole) of sodium nitrite in 10 ml of water was added to a hot solution of 2.7 g (0.01 mole) of 3-phenyl-4,5-dichloro-1,2,3-thiadiazolium chloride in 20 ml of 50% ethanol. The dark-yellow precipitate was filtered, and recrystallized from a benzene–heptane (1:1) mixture. Yield, 81%, mp 175-176°C [4]. Mass spectrum: M^+ 223. IR spectrum: 1660 cm^{-1} (C=O), UV spectrum, λ_{max} (log ε): 228 (3.82), 280 (3.4); 425 nm (4.03).

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DISULFIDES OF THE BENZO-2,1,3-THIADIAZOLE SERIES

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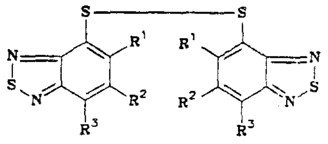
Disulfides of the benzo-2,1,3-thiadiazole series were obtained by reduction of benzo-2,1,3-thiadiazolesulfonyl chlorides (by hydriodic acid or by sulfur dioxide) or by the reaction of benzo-2,1,3-thiadiazolesulfinic acids with hydrogen bromide in acetic acid. Convenient methods for the synthesis of the starting compounds were found, and the fungicidal activity of the disulfides obtained was studied.

We have previously described a convenient method for the preparation of mercapto derivatives of benzo-1,2,3-thiadiazole from disulfides [1]. However, little is known about the syntheses and transformations of disulfides of the benzo-2,1,3-thiadiazole series [1-4]. In the present work these investigations are continued.

We showed that 4,4'-di(benzo-2,1,3-thiadiazolyl) disulfide (I), which we obtained previously [1] by the reaction of benzo-2,1,3-thiadiazole-4-sulfinic acid (II) with hydrogen bromide in glacial acetic acid, can be synthesized by the action of hydriodiodic acid on 4-chlorosulfonylbenzo-2,1,3-thiadiazole (III) in glacial acetic acid or by reduction of sulfonyl chloride III by sulfur dioxide in acetic acid in the presence of iodine.

Disulfides IV-VIII were synthesized in a similar way as disulfide I. The IR spectra of all these compounds contain the absorption band of the S–S group at 473-499 cm^{-1} (Table 1).



I, IV–VIII

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