RESEARCH ON 1,2-DITHIOLIUM DERIVATIVES

II.* OXIDATION OF ARYLHYDRAZONES OF DITHIOMESOXALIC ACID DIARYLAMIDES TO 1,2-DITHIOLIUM DERIVATIVES

L. N. Kulaeva, A. D. Grabenko,
and P. S. Pel'kis

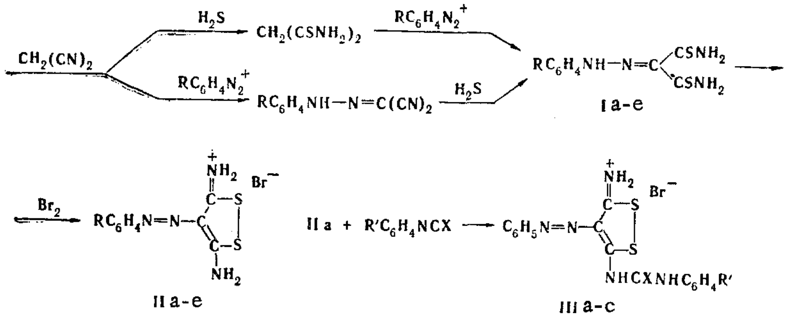
UDC 547.738

Arylazo derivatives of 3,5-diamino-1,2-dithiolium bromides were obtained by oxidation of arylhydrazones of dithiomesoxalic acid diamides with bromine in chloroform; the nonquaternized amino group of the products reacts with aryl iso(thio)cyanates to give the corresponding ureas and thioureas, regardless of the conditions.

We have previously studied the oxidation of dithiomalonic acid diarylamides with various oxidizing agents to give 3,5-diarylamino-1,2-dithiolium derivatives [1]. Of the 3,5-diamino-**1,2-dithiolium salts, 4-ethyl-,** phenyl, benzyl, and β-cyanoethyl derivatives with anions of hydrohalic acids are known [2, 3]. No data on 3,5-diamino-1,2-dithiolium salts with an arylazo or arylhydrazono group in the 4 position are available. Compounds of this type are of interest as potential physiologically active substances, since the dithiolium ring is included in the structures of the highly active antibiotics Thiolutin and Aureothricin [4].

1,2-Dithiolium 4-arylazo derivatives (II) cannot be obtained by coupling of 1,2-dithiolium derivatives with diazonium salts, since the 4 position of the 1,2-dithiolium ring is inert to electrophilic substitution. We synthesized II by oxidation of arylhydrazones of dithiomesoxalic acid diamides with bromine in chloroform.

Starting arylhydrazones Ia-e were obtained by coupling dithiomalonamide with arenediazonium salts or by reaction of malonic acid dinitrile with arenediazonium chlorides and subsequent saturation of alcohol solutions of arylhydrazones of mesoxalic acid dinitrile with hydrogen sulfide.



I a R=H; b R=p-CH_3; c R=o-CH_3; d R=o-CH_3O; e R=p-Cl. II a R=H; b R=p-CH_3, c R=o-CH_3; d R=o-CH_3O; e R=p-Cl. III a R′=p-CH_3, X=S; b R′=p-CH_3, X=S; c R′=H, X=O

The IR spectra of II contain intense characteristic absorption bands of an S—S bond in a five-membered dithiolium ring at 530-557 cm^{-1} [5] but do not contain absorption at 1150-1170 cm^{-1} (C=S). The intense bands at 1500-1580 cm^{-1} are characteristic for the N=N bond and the $\overset{+}{N}H_2$ group. The bands at 3430 and 3330 cm^{-1} correspond to the NH_2 group.

Compounds I are of independent interest, since the antimicrobial, pesticidal, and fungicidal activity of arylazo derivatives of malonic acid dinitrile is well known [6].

---

* See [1] for communication I.

Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev 252660. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 909-911, July, 1978. Original article submitted April 12, 1977; revision submitted November 21, 1977.

TABLE 1. Arylhydrazones of Mesoxalic Acid Dinitrile and Dithioamide $RC_6H_4NHN{=}CR'_2$

Compound	R	R′	mp, °C	Found, %		Empirical formula	Calc., %		Yield, %
				N	S		N	S	
—	p-CH_3	CN	169	30,3	—	$C_{10}H_8N_4$	30,4	—	63
—	o-CH_3	CN	99	30,2	—	$C_{10}H_8N_4$	30,4	—	50
—	o-CH_3O	CN	111	27,8	—	$C_{10}H_8N_4O$	28,0	—	51
—	p-Cl	CN	185	27,3	—	$C_9H_5N_4Cl$	27,4	—	53
Ia	H	$CSNH_2$	172	23,3	26,9	$C_9H_{10}N_4S_2$	23,5	26,9	70
Ib	p-CH_3	$CSNH_2$	178	22,1	25,3	$C_{10}H_{12}N_4S_2$	22,2	25,4	66
Ic	o-CH_3	$CSNH_2$	151	22,4	25,1	$C_{10}H_{12}N_4S_2$	22,2	25,4	68
Id	o-CH_3O	$CSNH_2$	158	21,0	23,9	$C_{10}H_{12}N_4S_2O$	20,8	23,9	63
Ie	p-Cl	$CSNH_2$	220 (dec.)	20,7	23,3	$C_9H_9N_4S_2Cl$	20,5	23,5	51

TABLE 2. Substituted 4-Arylazo-1,2-dithiolium Bromides II-III

Compound	R	R′	mp, °C	Found, %			Empirical formula	Calc., %			Yield, %
				Br	N	S		Br	N	S	
IIa	H	H	228	25,7	—	21,6	$C_9H_9BrN_4S_2$	25,2	—	21,9	69
IIb	p-CH_3	H	218	24,7	—	19,2	$C_{10}H_{11}BrN_4S_2$	24,2	—	19,3	79
IIc	o-CH_3	H	232	24,1	—	19,1	$C_{10}H_{11}BrN_4S_2$	24,2	—	19,3	74
IId	o-CH_3O	H	212	22,9	—	18,1	$C_{10}H_{11}BrN_4OS_2$	23,1	—	18,4	77
IIe	p-Cl	H	270	—	—	18,2	$C_9H_8BrClN_4S_2$	—	—	18,2	64
IIIa	H	$CSNHC_6H_5$	230	—	15,3	21,3	$C_{16}H_{14}BrN_5S_3$	—	15,4	21,2	51
IIIb	H	$CSNHC_6H_4CH_3$-p	173	—	14,9	20,5	$C_{17}H_{16}BrN_5S_3$	—	15,0	20,6	50
IIIc	H	$CONHC_6H_5$	224	—	16,3	14,4	$C_{16}H_{14}BrN_5OS_2$	—	16,3	14,7	62

Under the influence of nucleophilic agents, the synthesized 4-arylazo-3,5-diamino-1,2-dithiolium bromides (II) undergo opening of the dithiolium ring with the liberation of sulfur, as in the case of 3,5-diaryl-, dialkyl-, and diamino-substituted 1,2-dithiolium salts [2, 7, 8]. When there are arylamino groups in the 3 and 5 positions of the ring, the dithiolium derivatives are stable with respect to acids and bases.

Regardless of the conditions, the reaction of salts II with aryl iso(thio)cyanates proceeds only at one amino group to give 4-arylazo-3-[N-phenyl(thio)carbamoyl]amino-1,2-dithiolium bromides (III).

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-10 spectrometer. Thin-layer chromatography (TLC) was carried out on Silufol UV-254 plates under standard conditions at room temperature in butanol–acetic acid–water.

Mesoxalic Acid Dinitrile Phenylhydrazone. A 1-g sample of malonic acid dinitrile was dissolved in 30 ml of alcohol, and a solution of 6 g of sodium acetate in 15 ml of water was added, and the mixture was cooled with ice water and treated with stirring with a diazonium solution prepared from 1.4 g of aniline, 10 ml of HCl, 20 ml of water, and 1.1 g of $NaNO_2$ in 6 ml of water. After 1 h, the mixture was cooled and poured over 100 g of ice. The yellow precipitate was removed by filtration, washed with water, and air dried. The yield was 2.1 g (82%).

The compounds presented in Table 1 were similarly obtained.

Dithiomesoxalic Acid Diamide Phenylhydrazone (Ia). A) A 0.5-g sample of mesoxalic acid dinitrile phenylhydrazone was dissolved in 5 ml of alcohol, and the solution was cooled with ice water and saturated successively with ammonia for 40 min and with hydrogen sulfide for 3 h. The mixture was allowed to stand at room temperature for 17 h, after which it was diluted with water and acidified with HCl. The resulting yellow precipitate was removed by filtration, washed with water, and air dried. The yield was 0.53 g (70%).

B) A 0.8-g sample of dithiomalonamide was dissolved in 50 ml of alcohol, and a solution of 2.4 g of sodium acetate in 10 ml of water was added with stirring and ice cooling. A solution prepared from 0.54 g of aniline, 4 ml of HCl, 6 ml of water, and 0.42 g of sodium nitrite in 4 ml of water was added to the mixture. After 1 h, the mixture was poured over ice, and the resulting precipitate was removed by filtration, washed with water, and dried to give the product in 42% yield.

Compounds Ib-e (Table 1) were obtained by methods A or B.

4-Phenylazo-3,5-diamino-1,2-dithiolium Bromide (IIa). A 1-g sample of dithiomesoxalic acid diamide phenylhydrazone was dissolved in 20 ml of chloroform, and a solution of 0.6 g of bromine in 50 ml of chloroform was added slowly with stirring and cooling. A light-brown precipitate formed gradually. The mixture was allowed to stand at room temperature for 1-2 h, after which the precipitate was removed by filtration and washed with chloroform and ether. The yield was 1 g.

Compounds IIb-e (Table 2) were similarly obtained.

3-(N-Phenylthiocarbamoyl)-4-phenylazo-5-amino-1,2-dithiolium Bromide (IIIa). A 0.3-g sample of 4-phenylazo-3,5-diamino-1,2-dithiolium bromide was dissolved in 10 ml of methanol or ethanol, 0.24 g of phenyl isothiocyanate was added, and the mixture was heated at 80°C for 1 h, during which a precipitate formed. A small amount of the alcohol was removed by evaporation, and the precipitate was removed by filtration, washed with ether, and air dried. The yield was 0.2 g.

Compounds IIIb,c (Table 2) were similarly obtained.

LITERATURE CITED

1. A. D. Grabenko, L. N. Kulaeva, and P. S. Pel'kis, Khim. Geterotsikl. Soedin., No. 7, 924 (1974).
2. U. Schmidt, Ber., 92, 1171 (1959).
3. K. A. Jensen, H. R. Baccaro, and Buchardt, Acta Chem. Scand., 17, 163 (1963).
4. W. D. Celmer and J. A. Solomons, J. Am. Chem. Soc., 77, 2861 (1955).
5. L. Schotte, Arkiv Kemi, 9, No. 84, 299 (1956).
6. T. Zsolnai, Biochem. Pharmacol., 13, 285 (1964); U.S. Patent No. 3062635 (1962).
7. E. Uhlemann and B. Zollner, Z. Chem., 14, 245 (1974).
8. E. Uhlemann, K. H. Uteg, and B. Zollner, Z. Chem., 10, 468 (1970).

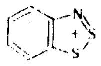
STRUCTURES AND REACTIVITIES OF BENZO-1,2,3-DITHIAZOLIUM SALTS AND THEIR SELENIUM ANALOGS

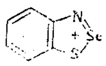
Yu. I. Akulin, M. M. Gel'mont,
B. Kh. Strelets, and L. S. Éfros

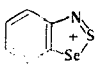
UDC 547.794

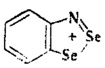
A number of benzo-1,2,3-dithiazolium chlorides (I) and their selenium analogs – benzo-1,2,3-thiaselenazolium, benzo-2,1,3-thiaselenazolium, and benzo-1,2,3-diselenazolium salts – were synthesized. The electronic structures and reactivities of the I cation and salts I-IV are discussed on the basis of a quantum-chemical calculation of cation I and the PMR spectra of salts I-IV. Successive substitution of the sulfur atoms in the I cation by selenium atoms, particularly in the 2 position, substantially increases the degree of transfer of positive charge to the condensed benzene ring. The trend of the nucleophilic reactivities of 6-methoxy derivatives of salts I-IV in the reaction with aromatic amines is the same as the trend of the degree of localization of the positive charge in the 6 position.

In our preceding communications we described the selenium analogs of benzo-1,2,3-dithiazolium salts (I), – benzo-1,2,3-thiaselenazolium (II), benzo-2,1,3-thiaselenazolium (III), and benzo-1,2,3-diselenazolium (IV) salts – and described some of their properties [1-4].


I


II


III


IV

Leningrad Branch, Design Scientific-Research Institute of Synthetic Fibers, Leningrad 195030. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 912-916, July, 1978. Original article submitted September 16, 1977.