1, 2-DITHIOLIUM SALTS

II. 1, 2-Dithiolium Salts of Inorganic, Heteroorganic, and Organic Acids*

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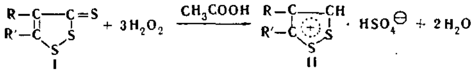
A new method for the synthesis of 1, 2-dithiolium hydrogen sulfates by the oxidation of 1, 2-dithiole-3-thiones with hydrogen peroxide in acetic acid has been developed. From 4-(p-tolyl)1, 2-dithiolium hydrogen sulfate a series of salts containing anions of inorganic, heteroorganic, and organic acids (Cl^-, Br^-, I^-, ClO_4^-, CNS^-, VO_3^-, $HMoOO_4^-$, $S_2O_3^{2-}$, $S_2O_8^{2-}$, $Cr_2O_7^{2-}$, $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, $B(C_6H_5)_4^-$, F_3CCOO^-, $C_6H_2(NO_2)_3O^-$) has been obtained. 4-(p- tolyl)-1, 2-dithiolium salts containing the anions NO_2^-, NO_3^-, ClO_3^-, BrO_3^-, SO_3^{2-}, SO_4^{2-}, $S_2O_5^{2-}$ and Cl_3CCOO^- dissolve in water and do not precipitate in double decomposition reactions. The reactions of 4-(p-tolyl)-1, 2-dithiolium hydrogen sulfate with sodium sulfite, disulfide, and hydrogen sulfide lead to the formation of bis[4-(p-tolyl)-1, 2-dithiol-3-yl] sulfide and disulfide and the sodium salt of 4-(p -tolyl-1, 2-dithiole-3-thiol, respectively. The reaction of 4-(p-tolyl)-1, 2-dithiolium hydrogen sulfate with solutions of salts of the alkali metals containing the anions of weak acids F^-, CNO^-, HCO_3^-, CO_3^{2-}, $B_4O_7^{2-}$, $HAsO_4^{2-}$, PO_4^{3-}, CH_3COO^-, $ClCH_2COO^-$, etc.) forms bis[4-(p-tolyl)-1, 2-dithiol-3-yl] oxide. [8, Table 3].

The most readily accessible 1, 2-dithiolium salts are the hydrogen sulfates (II). Up to now, only one method for their preparation was known, based on the oxidation of 1, 2-dithiole-3-thiones with peracetic acid in acetone [2, 3]. We have developed a simpler and more convenient method for oxidizing, 1, 2-dithiole-3-thiones to 1, 2-dithiolium hydrogen sulfates with a yield of up to 70% by a solution of hydrogen peroxide in acetic acid as follows:

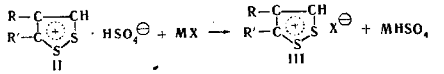


The maximum yields of II from 1, 2-dithiole-3-thiones having aromatic substituents in position 4 are found at a molar ratio of I to H_2O_2 of 1 : 2, a temperature of 100° C, and a reaction time of 3–4 hr. 1, 2-Dithiole-3-thiones substituted by an aryl group in position 5 oxidize considerable faster (the process is complete in 30–40 min). More prolonged heating leads to the cleavage of the 1, 2-dithiole heterocycle.

When the process is carried out in acetone, the yield of II is lower (46%), while an increase in the amount of H_2O_2 leads to the cleavage of the 1, 2-dithiole ring.

By the oxidation of I with hydrogen peroxide in acetic acid we have obtained a number of 4- and 5-aryl-1, 2-dithiolium hydrogen sulfates, information on which is given in Table 1.

In addition to 1, 2-dithiolium hydrogen sulfates, the chlorides, bromides, iodides, and perchlorates are mentioned in the literature [2–7]. These salts are insoluble in water and can therefore easily be obtained by means of the double decomposition of II with salts of the corresponding inorganic acids in water.



M = Na, K; X = acid anion

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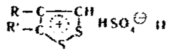
*For part I, see [1].

Table 1. 1,2-Dithiolium Hydrogen Sulfates  II

II		Decomp. p., °C	External form of the crystals	Empirical formula	Found, %			Calculated, %			Yield, %
R	R′				C	H	S	C	H	S	
C_6H_5	H	224,5	Light yellow needles	$C_9H_8O_4S_3$	38,80	3,17	35,28	39,11	2,91	34,81	46,2
p-$CH_3C_6H_4$	H	246	Lustrous lemon yellow plates	$C_{10}H_{10}O_4S_3$	41,43	3,56	33,36	41,36	3,47	33,12	69,2
p-$CH_3OC_6H_4$	H	242,5	Lustrous dark yellow plates	$C_{10}H_{10}O_5S_3$	39,39	3,61	31,83	39,20	3,29	31,39	61,5
p-ClC_6H_4	H	241	Lemon yellow needles	$C_9H_7O_4S_3Cl$	34,73	2,42	30,91	34,85	2,26	30,95	44,1
H	p-$CH_3OC_6H_4$	222	Lustrous green plates	$C_{10}H_{10}O_5S_3$	39,17	3,41	31,25	39,20	3,29	31,39	67,3

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*The same abbreviation is used in subsequent schemes.

By this method we have obtained a number of 4-(p-tolyl)-1,2-dithiolium salts containing anions of inorganic, heteroorganic, and organic acids (Cl^-, Br^-, J^-, CNS^-, VO_3^-, $HMoO_4^-$, $S_2O_3^{2-}$, $S_2O_8^{2-}$, $Cr_2O_7^{2-}$, $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, $B(C_6H_5)_4^-$, F_3CCOO^-, $C_6H_2(NO_2)_3O^-$).

All these salts are well-crystalline brightly-colored water-insoluble substances (Table 2).

Table 2. 4-(p- tolyl) 1, 2-dithiolium Salts

$Dt_n^+ X^{n-} \cdot mH_2O$*

X	n	m	Mp, °C**	Color and form of the crystals	Empirical formula	Found, %				Calculated, %			
						C	H	S	N	C	H	S	N
Cl	1	2	192—193	Light yellow needles	$C_{10}H_{13}O_2S_2Cl$	45,27	4,79	24,26		45,36	4,93	24,21	
Br	1	1	>220	Yellow needles	$C_{10}H_{11}OS_2Br$	41,51	3,69	22,19		41,24	3,80	22,01	
I	1	0	123—124	Bright orange plates	$C_{10}H_9S_2I$	37,29	2,40	20,06		37,50	2,83	20,02	
ClO_4	1	0	218,5	Yellow needles	$C_{10}H_4O_4S_2Cl$	41,11	3,09			41,06	3,08	21,93	
CNS	1	0	160,5	Bright yellow plates	$C_{11}H_9S_3N$	52,67	3,58	38,67	5,40	52,53	3,61	38,22	5,57
VO_3	1	6	>210	Green	$C_{10}H_{21}O_9S_2V$	30,54	5,53	16,03		30,00	5,28	16,01	
$HMoO_7$	1	7	>200	Light yellow	$C_{10}H_{24}O_{11}S_2Mo$	25,37	5,09	12,72		25,00	5,03	13,35	
$B(C_6H_5)_4$	1	0	130—131	Light yellow	$C_{34}H_{29}S_2B$	78,96	5,32	12,46		79,52	5,69	12,48	
S_2O_3	2	0	>210	Orange	$C_{20}H_{18}O_3S_6$	48,20	3,71	38,04		48,16	3,62	38,57	
S_2O_8	2	0	>200	Light yellow needles	$C_{20}H_{18}O_8S_6$	41,17	3,03	33,28		41,52	3,13	33,26	
Cr_2O_7	2	0	>260	Yellow	$C_{20}H_{18}O_7S_4Cr_2$	40,03	3,06	21,50		39,86	3,01	20,28	
$Fe^{III}(CN)_6$	3	4	212—214	Yellow-green	$C_{36}H_{35}O_4S_6N_6Fe$	50,17	4,22	22,43	9,84	50,05	4,08	22,27	9,72
$Fe^{II}(CN)_6$	4	8	196—197	Black	$C_{46}H_{52}O_8S_8N_6Fe$	49,19	3,91	22,15	12,21	48,92	4,64	22,71	7,44
CF_3COO	1	0	128—129	Light yellow needles	$C_{12}H_9O_2S_2F_3$	47,15	3,21	20,76		47,05	2,96	20,93	
2,4,6-$(O_2N)_3C_6H_2O$	1	0	158—159	Bright yellow	$C_{16}H_{12}O_7S_2N_3$	45,47	3,02	15,31	11,09	45,49	2,86	15,18	9,97

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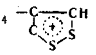
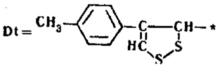
* Dt=p-$CH_3C_6H_4$ 

** Apart from $Dt[B(C_6H_5)_4]$, $Dt[OOCCF_3]$andDt$[OC_6H_2(NO_2)_3]$, all the compounds melted with decomposition, and $DtClO_4$ explosively.

When 4-(p-tolyl)-1,2-dithiolium hydrogen sulfate (IV) reacts with such anions as NO_2^-, NO_3^-, ClO_3^-, BrO_3^-, SO_3^{2-}, SO_4^{2-}, $S_2O_5^{2-}$, Cl_3CCOO^-, no precipitates of the corresponding salts are formed, which shows that they are soluble in water. When the double-decomposition reaction of IV with anions of weak acids is carried out, i.e., using aqueous solutions of alkali-metal salts having pH values above 7 (F^-, CNO^-, HCO_3^-, CO_3^{2-}, $B_4O_7^{2-}$, $HAsO_4^{2-}$, PO_4^{3-}, CH_3COO^-, $ClCH_2COO^-$, ICH_2COO^-), salts of type III are formed. In all these cases a bright yellow precipitate of bis[4-(p-tolyl)-1,2-dithiol-3-yl]oxide (V) precipitates:

$ClCH_2COO^-$, ICH_2COO^-),

$$\underset{IV}{Dt^+[HSO_4]^-} + 2OH^- \longrightarrow \underset{V}{Dt_2O} + H_2O + 2HSO_4^-$$



Apparently, an intermediate in this reaction is 4-(p-tolyl)-1,2-dithiolium hydroxide (VI), which then undergoes anhydrocondensation to give V.

$$\underset{IV}{Dt^+[HSO_4]^-} + OH^- \longrightarrow \underset{VI}{DtOH} + HSO_4^-$$

The structure of V was confirmed by the analytical results and a determination of its molecular weight, by the absence of active hydrogen (i.e., an OH group), and by its conversion into the corresponding 1,2-dithiolium chloride (VII) by the action of hot concentrated hydrochloric acid (yield 82.7%) or of hydrogen chloride in benzene (yield 83.5%).

$$\underset{V}{Dt_2O} + 2HCl \longrightarrow \underset{VII}{2Dt^+Cl^-} + H_2O$$

The reaction of 4-(p-tolyl)-1,2-dithiolium hydrogen sulfate with sodium sulfide and disulfide formed, respectively bis[4-(p-tolyl)-1,2-dithiol-3-yl] sulfide Dt_2S (VIII) and the disulfide Dt_2S_2 (IX).

$$2Dt^+[HSO_4]^- + Na_2S_n \longrightarrow \underset{VIII\ n=1,\ IX\ n=2}{DtS_nDt} + 2NaHSO_4$$

The action of hydrogen chloride in benzene on VIII and IX also converted them into 4-(p-tolyl)-1,2-dithiolium chloride (VII) with the simultaneous liberation of hydrogen sulfide:

$$\underset{VIII}{Dt_2S} + 2HCl \longrightarrow \underset{VII\ (89\%)}{2Dt^+Cl^-} + H_2S$$

The reaction of 4-(p-tolyl)-1,2-dithiolium hydrogen sulfate (IV) with sodium hydrogen sulfide gave the sodium salt of 4-(p-tolyl)-1,2-dithiole-3-thiol (X):

$$Dt^+[HSO_4]^- + 2NaSH \longrightarrow \underset{X}{DtSNa} + NaHSO_4 + H_2S$$

The behavior of compounds V, VIII, IX, and X differed somewhat from that of 1,2-dithiolium salts of the type of $Dt_n^+X^{n-}$. The question of their fine structure will be considered subsequently with the publication of the results of IR and PMR spectroscopy and of investigations by other physical and chemical methods.

The results that we have obtained show that 1,2-dithiolium hydrogen sulfates may find use in analytical chemistry for the detection, determination, and separation of various anions. We shall devote a separate communication to this question.

EXPERIMENTAL

4-(p-tolyl)-1,2-dithiolium hydrogen sulfate (IV). A solution of 1.0 g (4.5 mM) of 4-(p-tolyl)-1,2-dithiole-3-thione (Ia) and 1 ml of 30% hydrogen peroxide (9 mM) in 10 ml of glacial acetic acid was heated in the boiling water bath for 3 hr and was left overnight at room temperature. The lustrous lemon yellow plates of IV that had deposited were filtered off with suction, washed with benzene, and dried. Yield 0.9 g (69.2%), decomp. p. 245–246° C.

4-(p-tolyl)-1,2-dithiolium chloride dihydrate ($VII \cdot 2H_2O$). An excess of a 20% aqueous sodium chloride solution was added to a 2% aqueous solution of 1.0 g (3.5 mM) of IV. The light yellow acicular crystals of $VII \cdot 2H_2O$ that deposited were filtered off with suction, washed with water and ethanol, and dried in vacuum. Yield 0.52 g (57.1%), decomp. p. 193° C.

The other 4-(p-tolyl)-1,2-dithiolium salts were obtained similarly (see Table 3).

Table 3. 3-Substituted 1,2-Dithioles*

Compound	Mp, °C	Color	Empirical formula	Found, %			Calculated, %		
				C	H	S	C	H	S
Dt_2O	52—53	Bright yellow	$C_{20}H_{18}OS_4$	59,75	4,44	31,45	59,71	4,48	31,88
Dt_2S	112—113	Yellow	$C_{20}H_{18}S_5$	57,27	4,21	38,77	57,37	4,31	38,29
Dt_2S_2	95—96	Yellow	$C_{20}H_{18}S_6$	53,19	3,89	42,64	53,32	4,00	42,65
DtSNa	200	Yellow-brown	$C_{10}H_9S_3Na$	47,82	3,93	38,29	48,36	3,69	38,73

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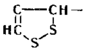
* Dt = p-$CH_3C_6H_4$ 

Bis[4-(p-tolyl)-1,2-dithiol-3-yl] oxide (V). An excess of a 20% aqueous solution of sodium bicarbonate was added to a 2% aqueous solution of 1.0 g (3.5 mM) of IV. The bright yellow precipitate that deposited was filtered off with suction, washed with water, and dried in vacuum. Yield 0.59 g (83.5%), mp 52–53° C. Found, mol. wt. 409. $C_{20}H_{18}S_4O$. Calculated: mol. wt. 402.62.

Bis[4-(p- tolyl)-1, 2-dithiol-3-yl] sulfide (VIII). This was obtained similarly by the reaction of IV and Na_2S in water. Yield 94.5%, mp 112–113° C.

Bis[4-(p-tolyl)-1,2-dithiol-3-yl] disulfide (IX). This was obtained in a similar manner to VIII by the reaction of IV with Na_2S_2 in water. Yield 96.2%, mp 95–96° C.

Sodium salt of 4-(p-tolyl)-1,2-dithiole-3-thiol (X). This was obtained by the reaction of IV with sodium hydrogen sulfide in water. Yield 59.7%. It decomposes on being heated above 200° C.

ADDITION AT THE PROOF-READING STAGE

After the preparation of this paper for the press, a paper became known to us in which the conversion of 4-phenyl-1,2-dithiolium hydrogen sulfate into compounds with structures analogous to V and VIII is described [8].

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