

## HYDROLYSIS OF 4,5-DIARYL- AND 4-ARYL-1,3-DITHIOLIUM PERCHLORATES

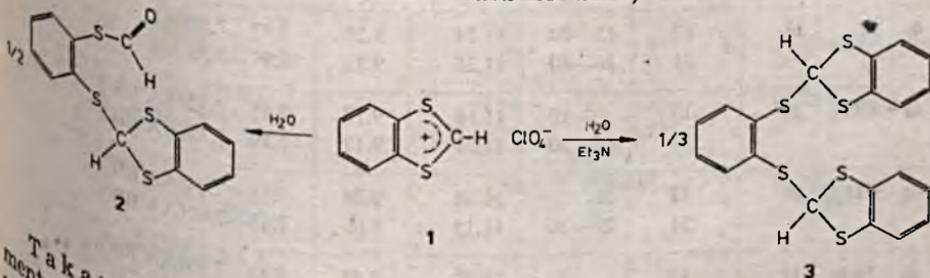
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Zbadano reakcję hydrolizy nadchloranów 4,5-diarylo- oraz 4-arylo-1,3-ditioliowych (4a-h) stwierdzając, że głównymi jej produktami są odpowiednie zasady karbinolowe 5. Trzy z tych karbinoli, tj. 5a, 5b i 5h wyodrębniono, w pozostałych przypadkach powstawanie 2-hydroksy-związków udokumentowano metodami spektralnymi. Przedyskutowano przebieg hydrolizy soli 4 oraz rozważono przemiany tautomeryczne, jakim mogą ulegać karbinole 5.

Hydrolysis of 4,5-diaryl- and 4-aryl-1,3-dithiolium perchlorates (4a-h) has been investigated. It was stated that corresponding carbinol bases 5 were the main products of these reactions. Three carbinols, i.e. 5a, 5b and 5h, were isolated, in other cases formation of the 2-hydroxy compounds was evidenced by spectral methods. The course of hydrolysis of salts 4 and, particularly, the tautomerism of carbinol bases 5 were discussed.

We have reported previously<sup>1-3</sup> that hydrolysis of benzo-1,3-dithiolium perchlorate (1), depending on the reaction conditions, leads to formation of the intermediate 2 or 3. On the basis of spectral evidences (<sup>1</sup>H NMR and IR) nevertheless this compound has not been isolated. It may be assumed that hydrolysis of salt 1 does not stop at the stage of formation of the 2-hydroxy compound (i.e. the so-called carbinol base).



Takamizawa and Hirai<sup>4,5</sup> assume, on the basis of UV measurements, that 1,3-dithiolium salts with aryl substituents occur in aqueous solutions in equilibrium with the corresponding carbinols. The correctness of this assumption was confirmed by isolation of 2-hydroxy-4-phenyl-1,3-dithiol from the reaction of 4-phenyl-1,3-dithiolium hydrosulfate with

water<sup>4</sup>). However, the authors did not give a full characteristics of the product obtained.

In this paper we wish to present the results obtained by treatment with water of 1,3-dithiolium perchlorates containing various aryl groups (4a—h).

## RESULTS

Hydrolysis of 4,5-diaryl- and 4-aryl-1,3-dithiolium perchlorates (4a—h) was carried out in two different ways: (1) in a heterogeneous system: by treatment of salt 4 with an appreciable excess of water and simultaneous extraction of the reaction products with carbon tetrachloride; (2) in a homogeneous system: by treatment of salt 4 in acetonitrile solution with a moderate excess of water. In both cases the perchloric acid liberated in the reaction renders the solution acidic. Proceeding in accordance with method (1) we were only able to isolate the products of hydrolysis of salts

<sup>1</sup>H NMR spectra of solutions of 4,5-diaryl and 4-aryl-1,3-dithiolium perchlorates (4a—h) in

1,3-Dithiolium salt			Moles of H <sub>2</sub> O per 1 mole of salt 4	Degree of hydrolysis (%) <sup>a</sup>	Chemical shifts of protons ( $\delta$ , ppm) of 1,3-dithiolium salt 4		
No	R <sup>1</sup>	R <sup>2</sup>			H—C-2 <sup>b</sup>	H—C-5 <sup>b</sup>	H <sub>aromatic</sub>
4a	H	C <sub>6</sub> H <sub>5</sub>	17	ca. 30	11.22(s)	—	7.46(s)
			100	60	11.34(s)	—	7.47(s)
4b	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	17	20—30	11.20(s)	—	7.46(s); 7.28(s)
			100	50—60	11.28(s)	—	7.44(s); 7.27(s)
4c	CH <sub>3</sub> O	C <sub>6</sub> H <sub>5</sub>	17	10—15	11.17(s)	—	7.48(s); 7.40—6.93(AA'BB')
			100	ca. 50	11.24(s)	—	7.44(s); 7.41—6.94(AA'BB')
4d	NO <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>	17	50	11.43(s)	—	8.37—7.71(AA'BB'); 7.53(s)
			100	100	—	—	—
4e	H	H	17	15—20	11.24	9.23	7.92—7.53(m)
			51	30—40	11.25	9.23	7.99—7.58(m)
4f	CH <sub>3</sub>	H	17	10	11.18	9.18	7.85—7.32(AA'BB')
			51	ca. 30	11.21	9.17	7.79—7.35(AA'BB')
4g	CH <sub>3</sub> O	H	17	ca. 10	11.08	9.08	7.84—7.04(AA'BB')
			51	20—30	11.15	9.09	7.85—7.05(AA'BB')
4h	NO <sub>2</sub>	H	17	50	11.29	9.41	8.43—7.99(AA'BB')
			51	100	—	—	—

a Estimated on the basis of integration of appropriate spectral signals.

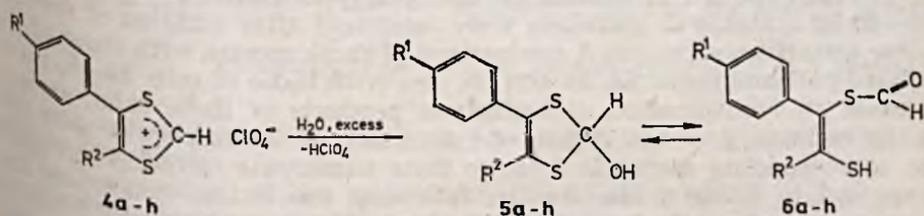
b In the case of salts 4e—h these protons give rise to an AX doublet signals,  $J = 3$  Hz.

c All these signals are singlets.

d Not visible.

e Only one part of AA'BB' system is visible.

4a and 4b, i.e. 2-hydroxy-4,5-diphenyl-1,3-dithiol (5a) and 2-hydroxy-4-phenyl-5-(*p*-tolyl)-1,3-dithiol (5b), whereas the hydrolysis in a homogeneous system gave only one hydroxy derivative, i.e. 2-hydroxy-4-(*p*-nitrophenyl)-1,3-dithiol (5h). In the remaining cases pure carbinols 5 were not obtained although the spectra of crude reaction mixtures support their formation.



	a	b	c	d	e	f	g	h
R <sup>1</sup> =	H	CH <sub>3</sub>	CH <sub>3</sub> O	NO <sub>2</sub>	H	CH <sub>3</sub>	CH <sub>3</sub> O	NO <sub>2</sub>
R <sup>2</sup> =	C <sub>6</sub> H <sub>5</sub>	H	H	H	H			

le 1  
CH<sub>3</sub>CN—H<sub>2</sub>O (homogeneous hydrolysis)

of hydrolysis product 5			Other signals
Aromatic	H—C-5°	H—C-2°	
7.21(s) 7.20(s)	— —	6.41 6.40	4.42 } OH 4.7 }
7.19(s); 7.03(s) 7.19(s); 7.03(s)	— —	6.39 6.40	
7.21(s); 7.18—6.74(AA'BB')	—	6.40	3.83 CH <sub>3</sub> O
7.20(s); 7.17—6.73(AA'B'B)	—	6.41	
8.15—7.4(AA'BB'); 7.32(s) 8.15—7.4(AA'BB'); 7.32(s)	—	6.57 6.57	
7.50—7.26(m) 7.52—7.28(m)	6.64 6.63	d 6.57	10.02 CHO
7.36—7.09(AA'BB')	6.64	6.56	10.20 } CHO 10.17 }
7.38—7.08(AA'BB')	6.64	6.55	
6.95—6.71° 7.47—6.79(AA'BB')	several signals <sup>d</sup> 6.62—6.2		10.20 } CHO 10.25 }
8.23—7.58(AA'BB')	6.99	6.71	
8.25—7.63(AA'BB')	7.05	6.77	

Thus one may presume that the primary products of hydrolysis of salts **4** are the so-called carbinol bases, i.e. 2-hydroxy-1,3-dithiols **5**, which are, however, rather unstable compounds. Some of these carbinols easily undergo spontaneous ring-opening and, therefore, their isolation and subsequent purification is somewhat cumbersome and not always successful.

<sup>1</sup>H NMR spectra of 4,5-diaryl- and 4-aryl-1,3-dithiolium perchlorate salts (**4a—h**) in acetonitrile solutions were measured after addition of definite molar quantities of water. A comparison of these spectra with those of isolated carbinol bases **5a**, **5b** and **5h**, and with those of salts **4a—h**, made possible an identification of hydrolysis products of these salts, as well as the estimation of the degree of conversion of the respective salts into the corresponding carbinols **5** (or to their tautomeric forms). The results presented in Table 1 lead to the following conclusions concerning the homogeneous hydrolysis of salts **4a—h**: (i) The hydrolysis of 4,5-diaryl- and 4-aryl-1,3-dithiolium perchlorates in acetonitrile solution in presence of liberated perchloric acid does not proceed to the completion even with relatively large molar excess of water (50 or 100 mole per 1 mole of salt). Only the hydrolysis of salts **4d** and **4h**, containing a nitro group in the aromatic ring, goes to completion in presence of a large excess of water.

Table 2

IR spectra of products of heterogeneous hydrolysis of 4,5-diaryl- and 4-aryl-1,3-dithiolium perchlorate salts (**4a—h**) in CCl<sub>4</sub>

1,3-Dithiolium salt			Characteristic stretching vibrations (in cm <sup>-1</sup> ) of the hydrolysis products <sup>a</sup>						
No	R <sup>1</sup>	R <sup>2</sup>	ν <sub>O-H</sub> (free)	ν <sub>O-H</sub> (ass.)	ν <sub>C-H</sub>	ν <sub>C-H</sub> (formyl)	ν <sub>S-H</sub>	ν <sub>C=O</sub>	ν <sub>NO<sub>2</sub></sub>
4a	H	C <sub>6</sub> H <sub>5</sub>	3570(m)	3360(v)	3080(s)	2835(w)	—	1695(s)	—
4b	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	3575(m)	3400(v)	3035(m) 2930(m)	2870(m)	—	1690(s)	—
4c	CH <sub>3</sub> O	C <sub>6</sub> H <sub>5</sub>	3555(m)	3400(v)	3100(w) 2965(w)	2845(m)	—	1690(s)	—
4d	NO <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>	3570(m)	3460(v)	3075(m) 2960(m)	2865(m)	2460(w)	1695(s)	1520(s) 1345(s)
4e	H	H	3570(w)	3370(v)	3040(m) 3070(m)	2840(m)	—	1690(s)	—
4f	CH <sub>3</sub>	H	3570(s)	3360(v)	3025(m) 2920(m)	2840(m)	—	1680(s)	—
4g	CH <sub>3</sub> O	H	3570(w)	3350(v)	3010(m) 2950(m)	2840(m)	—	1680(s)	—
4h	NO <sub>2</sub>	H	3570(w)	—	2970(m)	2860(w)	—	1690(m)	1537(s) 1355(s)

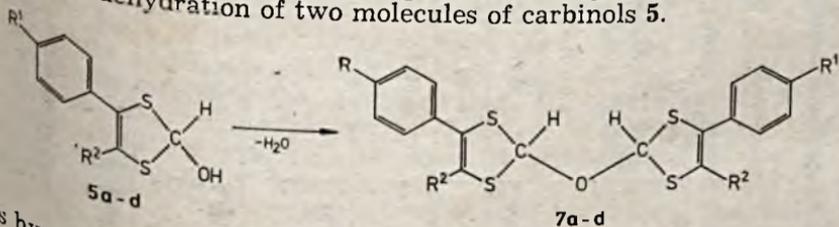
<sup>a</sup> Symbols in parentheses characterize the intensity of bands: (s) — strong, (m) — medium, (w) — weak, (v) — variable.

resulting in corresponding carbinols **5d** and **5h**. (ii) The homogeneous hydrolysis of 4,5-diaryl perchlorates (**4a—d**) stops at the stage of the corresponding 2-hydroxy-4,5-diaryl-1,3-dithiols (**5a—d**), whereas 2-hydroxy-4-aryl-1,3-dithiols (**5e—h**), resulting from the hydrolysis of monoaryl perchlorates (**4e—h**), undergo as a rule, opening of the hetero-ring affording compounds **6**. This fact is evidenced by  $^1\text{H}$  NMR spectra displaying at ca. 10 ppm<sup>2,3)</sup> the characteristic signal of the formyl proton

of the  $-\text{S}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$  grouping. Only 2-hydroxy-4-(*p*-nitrophenyl)-1,3-dithiol (**5h**) does not undergo tautomeric change under the conditions of homogeneous hydrolysis.

The composition of the reaction mixtures obtained by the heterogeneous hydrolysis perchlorates **4a—h** was estimated approximately on the basis of IR and  $^1\text{H}$  NMR spectra of the carbon tetrachloride extracts. The results of these measurements are given in Tables 2 and 3; they may be summarized as follows: (i) The heterogeneous hydrolysis of 4,5-diaryl- as well as 4-aryl-1,3-dithiolium salts leads to formation of corresponding

2-hydroxy-1,3-dithiols and of compounds containing a  $-\text{S}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$  group being undoubtedly products of the opening of the hetero-ring (i.e. compounds **6a—h**). (ii) It may be assumed that the heterogeneous hydrolysis of diaryl salts (**4a—d**) leads to formation, besides carbinols **5** and compounds **6**, also to formation of compounds **7** being, in all probability, the products of dehydration of two molecules of carbinols **5**.



This hypothesis is based on the presence of signals in the region of  $\delta$  6.5—6.7 (Table 3) in the  $^1\text{H}$  NMR spectra of the heterogeneous hydrolysis products of salts **4a—d**\*. It is the region of resonance of the methine proton in the  $\text{H}-\text{C}-\text{OCH}_3$  grouping of 2-methoxy-4,5-diphenyl-1,3-dithiol<sup>6</sup>.

### DISCUSSION

We believe that the compounds with the thioformyl grouping  $-\text{S}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$  are formed from 2-hydroxy-1,3-dithiols **5** as a result of the following tautomeric changes:

\* In the case of hydrolysis products of salts **4e—h** this region in  $^1\text{H}$  NMR spectra is undecipherable.

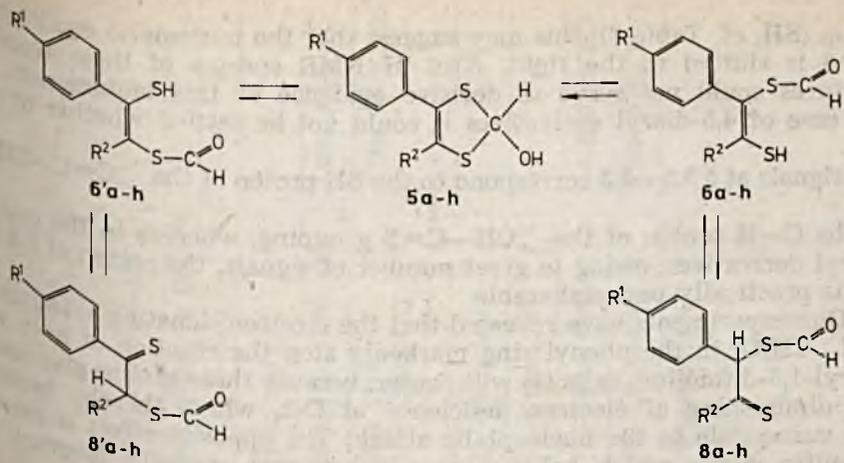
Table 3

<sup>1</sup>H NMR spectra of products formed in the heterogeneous hydrolysis of 4,5-diaryl- and 4-aryl-1,3-dithiolium perchlorates (4a-h) in CCl<sub>4</sub><sup>a</sup>

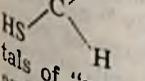
1,3-Dithiolium salt		Chemical shifts (δ, ppm) and intensities (in mm) of signals							
N <sub>0</sub>	R <sup>1</sup>	R <sup>2</sup>		H aromatic or H-C <sub>sp</sub> <sup>2</sup>				R <sup>1</sup> (CH <sub>3</sub> or CH <sub>3</sub> O)	
4a	H	C <sub>6</sub> H <sub>5</sub>	10.03(4)	7.13(185)	6.61(4)	6.32(6) <sup>b</sup>	5.32(4)	3.16(6) <sup>b</sup>	—
4b	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	10.06(4)	7.16—6.88(160)	6.58(5)	6.28(3) <sup>b</sup>	5.30(4)	2.98(3) <sup>b</sup>	2.26—2.22(50) <sup>c</sup>
4c	CH <sub>3</sub> O	C <sub>6</sub> H <sub>5</sub>	10.04(3)	7.53—6.57(179)	6.48(3)	6.24(5) <sup>b</sup>	5.33(3)	3.39(5) <sup>b</sup>	3.69—3.66(56) <sup>c</sup>
4d	NO <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>	10.00(4) 9.94(1)	8.05—7.09(161)	6.66(4)	6.36(18) <sup>b</sup>	5.45(1) 5.37(4)	4.00(18) <sup>b</sup>	—
4e	H	H	10.05(2) 10.00(6) 9.86(5)	7.95—7.17(183)	at least four signals in the region 6.3—5.7(28)				—
4f	CH <sub>3</sub>	H	10.05(2) 9.97(5) 9.63(7)	7.87—6.89(150)	at least five signals in the region 6.2—5.34(42)				2.52—2.21(92) <sup>c</sup>
4h	CH <sub>3</sub> O	H	10.11(5) 10.02(6)	8.08—6.71(108)	at least eight signals in the region 6.34—5.40(30)				3.73—3.70(75) <sup>c</sup>

<sup>a</sup> The products formed by hydrolysis of salt 4h are very hardly soluble in CCl<sub>4</sub>, hence the <sup>1</sup>H NMR spectrum could not be measured. These products give rise to broad aromatic signals.

<sup>b</sup> Intensities were measured in CCl<sub>4</sub> group at 40°C.

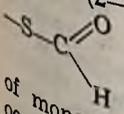


2-Hydroxy-1,3-dithiols **5** are cyclic esters of dithio-orthoformic acid



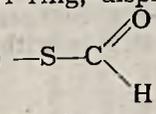
but they can be formally considered as hemimercap-

capitals of "mercaptoaldehydes" **6** (**6'**). From that point of view the opening and closing of the ring leading to the equilibrium state  $5 \rightleftharpoons 6$  (or  $6'$ ) consists in an intramolecular reaction of formation and cleavage of a cyclic hemimercaptal and represents an example of "ring-chain" tautomerism. In the case of carbinols having two different substituents (i.e.  $p\text{-R}^1\text{C}_6\text{H}_5 \neq \text{R}^2$ ) at  $\text{C}_4$  and  $\text{C}_5$  two isomeric "mercapto-aldehydes" may be formed (**6** and **6'**). Each of these "mercapto-aldehydes", being an enthiol compound, might undergo a subsequent tautomeric change of the type enthiol  $\rightleftharpoons$  thione affording the corresponding "thione-aldehydes" **8** and **8'**. There is not enough experimental evidence to determine conclusively the structure of the non-cyclic products of hydrolysis of 4,5-diaryl- and 4-aryl-1,3-dithiolium perchlorates (especially in a heterogeneous system).  $^1\text{H}$  NMR spectra of hydrolysis products of salts **4e-h** show the presence of several (2-3) signals corresponding to the formyl proton of the



grouping (Table 3) and, hence, we suppose that in the case

of monoaryl compounds ( $\text{R}^2 = \text{H}$ ) the opening of the 1,3-dithiol ring occurs, as a rule, in both directions, i.e.  $6' \rightleftharpoons 5 \rightleftharpoons 6$ . On the contrary, the spectra of the heterogeneous hydrolysis of diaryl compounds (**4a-c**), except salt **4d** with a nitro group in the phenyl ring, display only one signal corresponding to the formyl proton of the



grouping.

This suggests a one-way opening of the 1,3-dithiol ring. A tautomeric equilibrium enthiol  $\rightleftharpoons$  thione [**6** (**6'**)  $\rightleftharpoons$  **8** (**8'**)] for the compounds studied seems probable, but it cannot be considered as fully evidenced. Our hypothesis is based on the observation that IR spectra of mixtures resulting from heterogeneous hydrolysis of salts **4** do not generally display characteristic bands of the stretching vibrations of the thiol

group (SH, cf. Table 2); this may suggest that the tautomeric equilibrium  $6 \rightleftharpoons 8$  is shifted to the right. Also  $^1\text{H}$  NMR spectra of these reaction mixtures could not serve as decisive evidence of this tautomerism. In the case of 4,5-diaryl derivatives it could not be settled whether or not

the signals at  $\delta$  5.5—5.3 correspond to the SH proton of the  $\text{>C}=\overset{\text{SH}}{\text{C}}$  or to the C—H proton of the  $\text{>CH}-\overset{\text{S}}{\text{C}}$  grouping, whereas in the case of 4-aryl derivatives, owing to great number of signals, the region of  $\delta$  6.6—5.3 is practically undecipherable.

Our experiments have revealed that the electron-donating substituents ( $\text{CH}_3$ ,  $\text{CH}_3\text{O}$ ) in the phenyl ring markedly stop the reaction of aryl- and diaryl-1,3-dithiolium salts (4) with water, because these groups give rise to the diminishing of electron deficiency at C-2, which thereby becomes less susceptible to the nucleophilic attack. The opposite effect is exerted by nitro group which behaves as a substituent strongly favoring the reaction of salts 4 with water (cf. Table 1).

Finally, it should be emphasized that the 4,5-diaryl- and 4-aryl-1,3-dithiolium salts (4a—h) react with water somewhat more reluctantly than benzo-1,3-dithiolium perchlorate (1). As was stated previously<sup>3)</sup> an acetonitrile solution of salt 1 in presence of a 20-fold molar excess of water does not, practically, contain ( $^1\text{H}$  NMR assay) any dithiolium salt, whereas in the case of salts 4a—h under analogous reaction conditions (17 mole of water per 1 mole of salt) at most half of the salt undergoes hydrolysis. Moreover, it was observed that diaryl salts (4a—d) undergo hydrolysis somewhat more easily than the corresponding monoaryl salts (4e—h) as well that electron-withdrawing substituents in phenyl ring facilitate the reaction with water and the electron-donating ones have an opposite effect.

However, the more important difference in the behavior of mono- and diaryl-1,3-dithiolium salts towards water in comparison with that of the corresponding benzo compounds consists in the fact that in the case of the former compounds the reaction stops at the stage of forming carbinol bases 5, while in the case of the latter the reaction goes further to yield compounds 2 and 3 containing two or three substrate units. This difference in the behavior of the above salts may result from the fact that in the case of benzo-carbinols only one tautomeric equilibrium is possible, affording compounds with strongly nucleophilic groups attached to an aromatic ring. These compounds react easily with the strongly electrophilic benzo-1,3-dithiolium salt to yield compounds 2 or 3. On the other hand the mono- and diaryl carbinol bases are capable to undergo tautomeric changes in a much more complicated way leading to formation of more numerous and less stable products. This fact may induce the occurrence of various reactions which are difficult to anticipate and which may compete effectively with reactions leading to derivatives of type 2 and 3.

## EXPERIMENTAL

IR,  $^1\text{H}$  NMR and mass spectra as well as elemental analyses were performed at the Laboratory of Instrumental Analyses of Polytechnical University, Warszawa. IR spectra were recorded on UR-10 or Specord 71 IR spectrometers (Zeiss) and  $^1\text{H}$  NMR spectra — on Jeol JNM-MN-100 (TMS as internal standard). Mass spectra were taken with an LKB 9000 spectrometer (at 70 eV). Melting points are uncorrected.

Table 4

Characteristic data of 4,5-diaryl- and 4-aryl-1,3-dithiolium perchlorates (4a—h)

No	1,3-Dithiolium perchlorate	R <sup>1</sup>	R <sup>2</sup>	M.p. °C	<sup>1</sup> H NMR spectra (in CD <sub>3</sub> CN)			R <sup>1</sup>
					H—C-2 <sup>a</sup>	H—C-5 <sup>a</sup>	H <sub>aromatic</sub>	
4a	4,5-diphenyl-	H	C <sub>6</sub> H <sub>5</sub>	186—187	11.17(s, 1H)	—	7.45(s, 10H)	—
4b	4-phenyl-5-( <i>p</i> -tolyl)-	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	198—199	11.22(s, 1H)	—	7.49(s, 5H): 7.29(s, 4H)	2.93(s, 3H)(CH <sub>3</sub> )
4c	4-phenyl-5-( <i>p</i> -methoxyphenyl)-	CH <sub>3</sub> O	C <sub>6</sub> H <sub>5</sub>	165—166	11.08(s, 1H)	—	7.48(s, 5H); 7.33—6.59(m, 4H) <sup>b</sup>	3.78(s, 3H)(CH <sub>3</sub> O)
4d	4-phenyl-5-( <i>p</i> -nitrophenyl)-	NO <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>	178—179	11.25(s, 1H)	—	7.46(s, 5H); 8.24—7.67(m, 4H) <sup>b</sup>	—
4e	4-phenyl-	H	H	182—183	11.12(d, 1H)	9.18(d, 1H)	7.93—7.57(m, 5H)	—
4f	4-( <i>p</i> -tolyl)-	CH <sub>3</sub>	H	204—205	11.09(d, 1H)	9.14(d, 1H)	7.77—7.44(m, 4H) <sup>a</sup>	2.41(s, 3H)(CH <sub>3</sub> )
4g	4-( <i>p</i> -methoxyphenyl)-	CH <sub>3</sub> O	H	216—218	10.99(d, 1H)	9.03(d, 1H)	7.78—7.12(m, 4H) <sup>b</sup>	3.93(s, 3H)(CH <sub>3</sub> O)
4h	4-( <i>p</i> -nitrophenyl)-	NO <sub>2</sub>	H	166—167	11.24(d, 1H)	9.33(d, 1H)	8.40—8.06(m, 4H) <sup>b</sup>	—

<sup>a</sup> In the case of monoaryl salts 4e—h these protons give rise to an AX system ( $J = 3$  Hz).<sup>b</sup> These protons give rise to an AA'BB' system.

## Starting materials

4,5-Diaryl- and 4-aryl-1,3-dithiolium perchlorates (4a—h) were prepared according to<sup>7</sup>; their characteristic is presented in Table 4.

## Heterogeneous hydrolysis of salts 4a—h

A suspension of 1.4 mmole of perchlorate 4a—h in 30 ccm of water was shaken for 0.5 hr with 30 ccm of CCl<sub>4</sub> and the water layer was once more extracted with 15 ccm of CCl<sub>4</sub>. The combined extracts were washed with water, dried over MgSO<sub>4</sub> and evaporated to 2-ccm volume at room temperature (rotatory evaporator). IR and <sup>1</sup>H NMR spectra of the obtained solutions were measured. The results are collected in Tables 2 and 3.

The crude reaction mixtures were evaporated almost to dryness and allowed to stand for some time in a refrigerator. Crystalline products were obtained only in the case of salts 4a and 4b. After filtration and crystallization from CCl<sub>4</sub> the yields were:

(a) ca. 0.1 g (26%) of 2-hydroxy-4,5-diphenyl-1,3-dithiol (5a); colorless needles, m.p. 109—110°C (decomp. and evolution of gas); <sup>1</sup>H NMR (CCl<sub>4</sub>), δ: 7.14 (s, 10H, aromatic), 6.29 (d, AX, J = 11 Hz, 1H, H-C-2), 2.87 (d, AX, J = 11 Hz, 1H, O-H), IR (CCl<sub>4</sub>): 3375 cm<sup>-1</sup> (s, ν<sub>OH</sub>); MS, m/e: 272 (M<sup>+</sup>, 63%), 256 (99%), 210 (100%).

## Analysis:

For C<sub>15</sub>H<sub>12</sub>OS<sub>2</sub> — Calcd.: 66.1% C, 4.4% H, 23.5% S;

found: 66.1% C, 4.3% H, 23.1% S.

(b) ca. 0.1 g (25%) of 2-hydroxy-4-phenyl-5-(p-tolyl)-1,3-dithiol (5b); colorless crystals, m.p. 111—112°C (decomp. and evolution of gas); <sup>1</sup>H NMR (CCl<sub>4</sub>), δ: 7.95—6.88 (m, 9H, aromatic), 6.25 (d, AX, J = 11 Hz, 1H, H-C-2), 2.85 (d, AX, J = 11 Hz, 1H, O-H), 2.25 (s, 3H, CH<sub>3</sub>); IR (KBr): 3240 cm<sup>-1</sup> (s, ν<sub>OH</sub>).

## Analysis:

For C<sub>16</sub>H<sub>14</sub>OS<sub>2</sub> — Calcd.: 67.1% C, 4.9% H, 21.7% S;

found: 67.4% C, 5.0% H, 21.5% S.

## The homogeneous hydrolysis of salts 4a—h

<sup>1</sup>H NMR spectra measurements. Ca. 0.2 mmole of the appropriate salt 4 was dissolved in 1 ccm of a previously prepared mixture of acetonitrile and water. In the case of 4,5-diaryl-1,3-dithiolium perchlorates (4a—d) the content of water was: (a) ca. 17 mole per 1 mole of salt, and (b) ca. 100 mole per 1 mole of salt, whereas in the case of 4-aryl-1,3-dithiolium perchlorates (4e—h): (a) ca. 17 mole per 1 mole of salt, and (b) ca. 50 mole per 1 mole of salt. The results are shown in Table 1.

Attempts at isolation of the products: Water was added dropwise to a solution of 1 mmole of the appropriate salt 4 in 10—15 ccm of acetonitrile unless a slight turbidity is produced and stirring was continued for 0.5 hr at room temperature. Then more water was added to complete the precipitation of the product and the reaction mixture was cooled in a refrigerator. Only in the case of 4-(p-nitrophenyl)-1,3-dithiolium perchlorate (4h) a crystalline product was obtained. Attempts to purify the reaction product by crystallization have failed. The yield of crude 2-hydroxy-4-(p-nitrophenyl)-1,3-dithiol (5h) was ca. 0.2 g, m.p. 100—105°C (decomp. and evolution of gas); <sup>1</sup>H NMR (CD<sub>3</sub>CN), δ: 8.23 (m, AA'BB', 4H, aromatic), 7.0 (s, 1H, H-C-5), 6.70 (d, AX, J = 11 Hz, 1H, H-C-2), 5.44 (d, AX, J = 11 Hz, 1H, O-H); IR (KBr): 3400 (s, ν<sub>O-H</sub>), 1510 and 1342 cm<sup>-1</sup> (s, ν<sub>NO<sub>2</sub></sub>).

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