

HYDROLYSIS OF BENZO-1,3-DITHIOLIUM PERCHLORATE

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Zbadano reakcję hydrolizy nadchloranu benzo-1,3-ditioliowego w środowisku kwaśnym oraz w obecności Et_3N , stwierdzając dużą łatwość otwierania pierścienia ditioliowego w badanym układzie. Ustalono budowę produktów hydrolizy oraz zaproponowano mechanizm reakcji.

Исследовалась реакция гидролиза бенз-1,3-дителиолиевого перхлората в кислой среде и в присутствии Et_3N . Установлено отсутствие затруднений при открытии дителиолиевого кольца в исследуемой системе. Установлена структура получаемых продуктов гидролиза и предложен механизм реакции.

Hydrolysis of benzo-1,3-dithiolium perchlorate in acidic medium as well as in presence of Et_3N was investigated, and the great susceptibility to dithiolium ring-opening was stated. The products of hydrolysis were identified and the mechanism of their formation was proposed.

The considerable interest as regards olium salts containing quasi-aromatic five-membered rings with two hetero-atoms in 1,3-positions should be connected with the development of nucleophilic carbene chemistry, because these salts are used as precursors of carbenes. In our previous experiments¹⁾ concerning benzo-1,3-dithiolium perchlorate (**1**) as a source of benzodithiocarbene we observed an unusual susceptibility of this salt towards hydrolysis and we found that it reacted with water in a different manner than that accepted for thiazolium and oxazolium salts²⁾. As we have briefly reported³⁾ perchlorate **1** reacts with water in acidic medium giving *o*-(benzo-1,3-dithiolythio)phenyl thioformate (**2**), and not carbinol base **1a** which should be expected by analogy with the hydrolysis of other olium salts. This reaction proceeds smoothly and with very good yields, both when carried out in a heterogeneous system (by extraction of the product with organic solvent from aqueous suspension of **1**) and in solution (by precipitation of the product with water from solution of **1**).

In the present paper we wish to report the results of further investigations on hydrolysis of benzo-1,3-dithiolium perchlorate (**1**) in acidic medium as well as in presence of Et_3N .

RESULTS AND DISCUSSION

Hydrolysis in acidic medium

In order to investigate in more detail the course of hydrolysis of salt **1** it seemed useful to estimate the reaction mixture composition before the end-product (i.e. **2**) has been isolated. We achieved this purpose by comparing the NMR spectra of salt **1** in acetonitrile solutions containing various quantities of water with spectra of the substrate (Fig. 1) and the isolated product (Fig. 2).

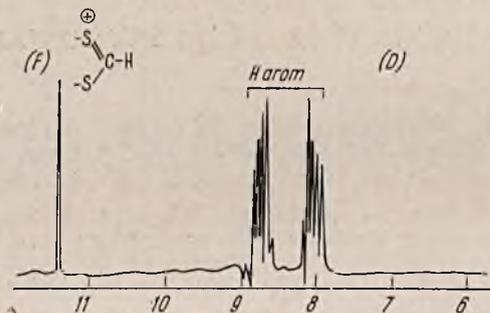


Fig. 1. NMR spectrum of benzo-1,3-dithiolium perchlorate (**1**) in anhydrous CH_3CN

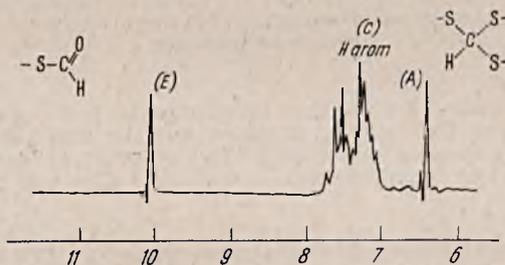


Fig. 2. NMR spectrum of *o*-(benzo-1,3-dithiolithio)phenyl thioformate (**2**) in anhydrous CH_3CN

It can be seen from the spectra presented in Figs 3—5 that, in addition to thioformate **2** (signals A, C and E) and possibly to the substrate (signals D and F), the reaction mixtures contain another hydrolysis product (singlet B at $\delta = 6.6$ and intensity of multiplet C). We believe that it is the carbinol base **1a** since the position of the singlet B is characteristic of C-2 protons of 2-alkoxyderivatives of 1,3-dithiol system (6.70 for C-2-H in 2-methoxybenzo-1,3-dithiol⁴⁾ and 6.64 for C-2-H in 2-methoxy-4,5-diphenyl-1,3-dithiol^{5,6)}). The intensity of the multiplet C evidently reveals that it must be derived from H_{arom} of both hydrolysis products (i.e. **2** and **1a**). From a simple calculation it follows that the total area of this multiplet (40) corresponds to eight aromatic protons of thioformate **2** ($3 \times 8 = 24$) and four aromatic protons of the carbinol base **1a** ($4 \times 4 = 16$; see integration of signals in Fig. 5).

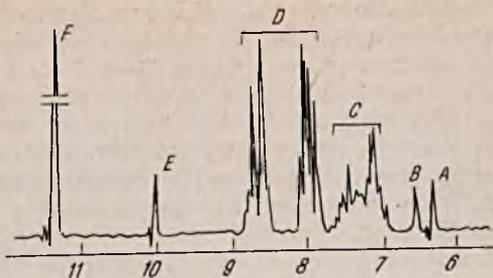


Fig. 3. NMR spectrum of benzo-1,3-dithiolium perchlorate (1) in CH_3CN in presence of 3 mole of water (per 1 mole of 1)

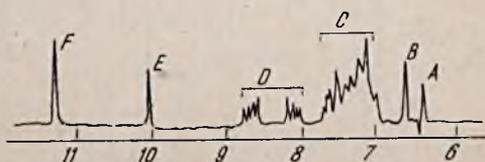


Fig. 4. NMR spectrum of benzo-1,3-dithiolium perchlorate (1) in CH_3CN in presence of 15 mole of water (per 1 mole of 1)

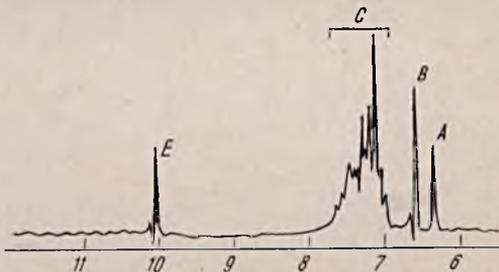


Fig. 5. NMR spectrum of benzo-1,3-dithiolium perchlorate (1) in CH_3CN in presence of 25 mole of water (per 1 mole of 1). The ratio of the integrated signals A, B, C and E is 3:4:40:3

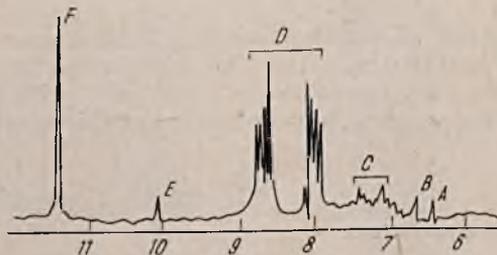
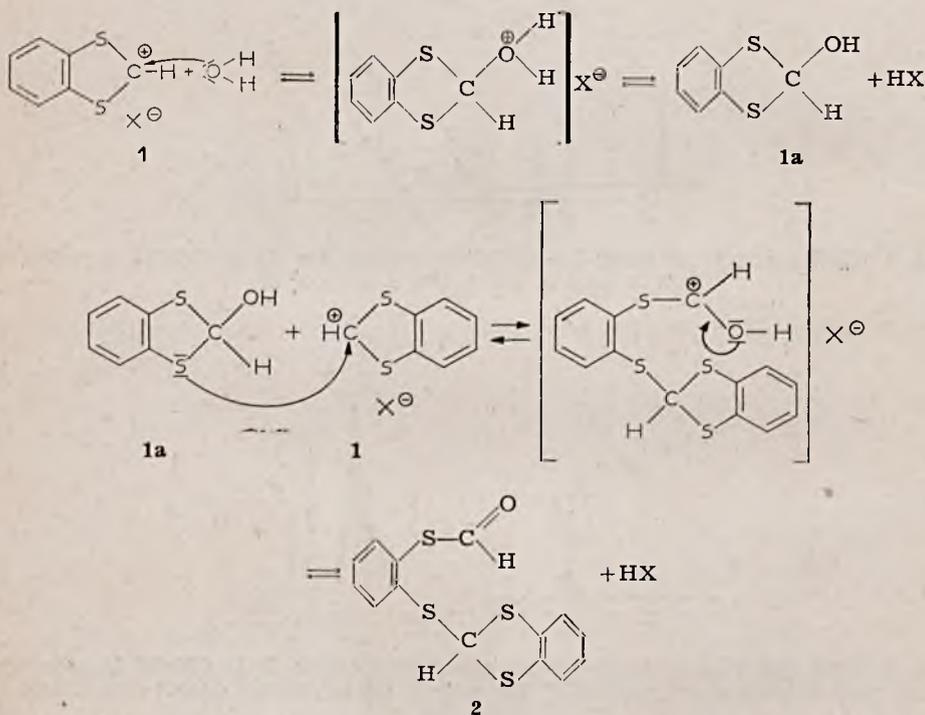


Fig. 6. NMR spectrum of benzo-1,3-dithiolium perchlorate (1) in CH_3CN in presence of 15 mole of water (per 1 mole of 1) after acidification with CF_3COOH

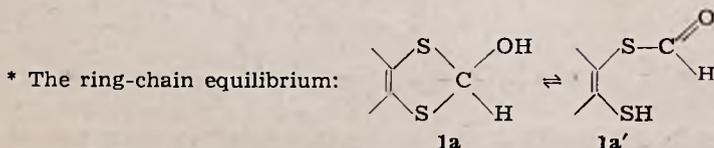
The above spectral measurements enabled us also to follow the progress of hydrolysis of **1** and revealed the reversibility of this reaction in acidic medium. From the spectra given in Figs 3—6 it can be seen that the degree of hydrolysis of salt **1** progresses with the increase of water content in the reaction mixture: with more than 25 mole of water the hydrolysis of substrate seems to be practically complete (Fig. 5). An additional acidification effects a displacement of the reaction equilibrium towards the substrate and with sufficient acid quantity the hydrolysis of salt **1** becomes markedly regressed (Fig. 6).

Taking into account the foregoing observations the course of hydrolysis of salt **1** in acidic medium may be formulated as in Scheme 1. The first reaction step involves, undoubtedly a nucleophilic attack of water molecule



Scheme 1

on the C-2 atom of dithiolium ring resulting in the formation of 2-hydroxybenzo-1,3-dithiol (carbinol base **1a**). This is followed by a further reaction of carbinol base **1a** (or its tautomeric form **1a'***) with salt **1** resulting in the heterocyclic ring-opening and formation of thioformate **2**. In a given



seems to be reasonable but it is not indicated by any experimental data.

solution of salt 1 containing some water and acid (liberated by hydrolysis of 1) an equilibrium between the substrate (1) and the hydrolysis products (1a and 2) has been established. The removal of one of the components from the reaction mixture (by precipitation or extraction of 2) results in the almost quantitative conversion 1 and 1a into 2 ($1 + 1a \rightarrow 2$, Scheme 1). Therefore, the initial hydrolysis product, i.e. carbinol base, is not isolated and thioformate 2 is the only product obtained by hydrolysis of salt 1.

According to Takamizawa and Hirai⁹, treatment of the 4-phenyl-1,3-dithiolium hydrogen sulfate (3) with water in heterogeneous conditions afforded 2-hydroxy-4-phenyl-1,3-dithiol (3a). It means that hydrolysis of salt 3 has been stopped on the carbinol base formation stage (Scheme 2).

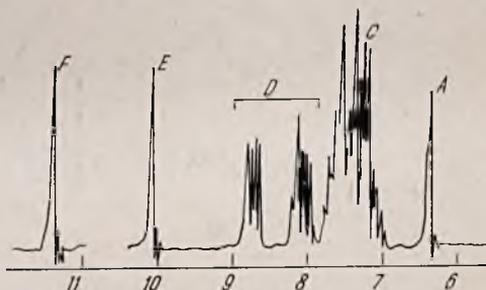
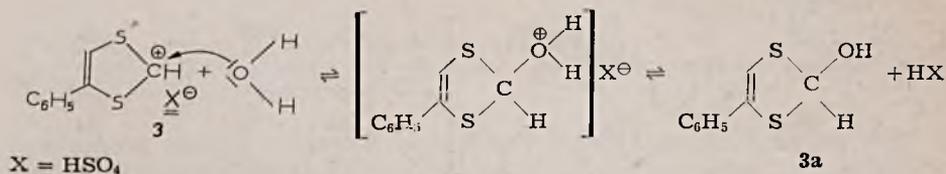


Fig. 7. NMR spectrum of *o*-(benzo-1,3-dithiolythio)phenyl thioformate (2) in anhydrous CH₃CN after acidification with CF₃COOH

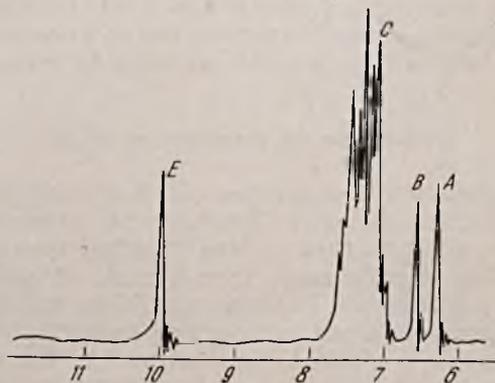
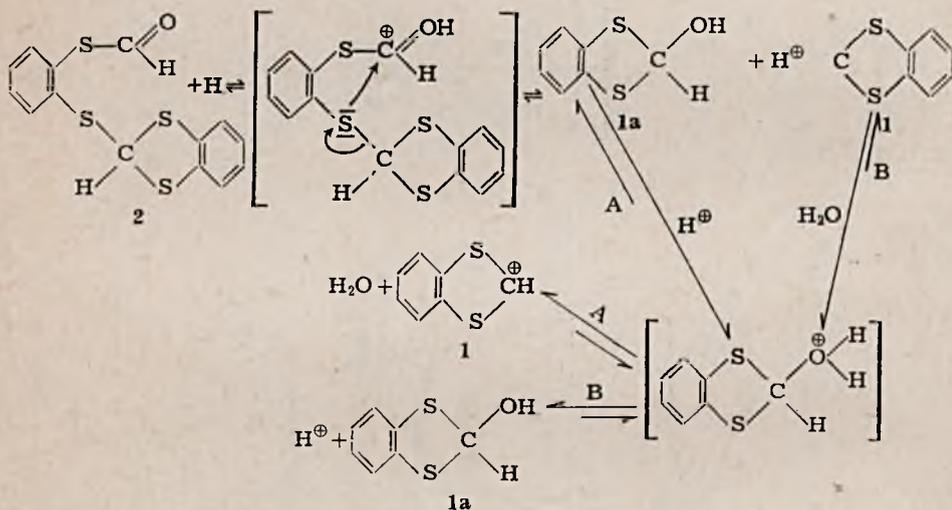


Fig. 8. NMR spectrum of *o*-(benzo-1,3-dithiolythio)phenyl thioformate (2) in CH₃CN in presence of water and acid

This different behaviour of dithiolium salts **1** and **3** under the same reaction conditions may be ascribed either to the more electrophilic character of benzo-1,3-dithiolium cation (salt **1**) as compared with 4-phenyl-1,3-dithiolium cation (salt **3**), or to a greater susceptibility of the fused-ring derivative to ring-opening⁷.

Thioformate **2** may be converted into dithiolium salt **1** by acidification of an anhydrous solution of **2**, while upon treatment of acidic solution of **2** with water carbinol base **1a** is produced. It was indicated by measuring NMR spectra of **2** in acetonitrile solution with addition of some water or acid, or both of them (Figs 7 and 8). The above transformations confirming the reversibility of the salt **1** hydrolysis may be formulated as in Scheme 3.



The cleavage of **2** into dithiolium salt **1** and carbinol base **1a** is facilitated by protonation. The carbinol base **1a** and dithiolium salt **1** can be interconverted into one another: anhydrous and acidic conditions (path A) are favourable to dithiolium cation formation but in presence of considerable amounts of water (path B) the reaction yielding **1a** becomes predominant.

Hydrolysis in presence of Et₃N

We found previously¹⁾ that *o*-di(benzo-1,3-dithiolythio)benzene (**4**) is produced in the reaction of salt **1** (1 mole) with water (15 mole), carried out with two mole of Et₃N. Now it is established that the same product is also formed using slightly more than 1 mole of amine and, to some extent, in neutral solution too. Reaction conditions and products obtained in the series of experiments are summarized in the Table.

The experiments a—c consisted in treatment of the substrate solution with water followed by addition of amine after several minutes; in experiment d—water together with amine was added into the solution of **1**, and in experiment e—the solution of **1** was added to the mixture of water

Table — Tablica

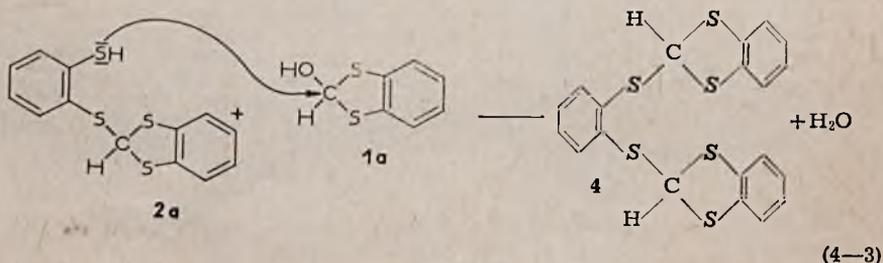
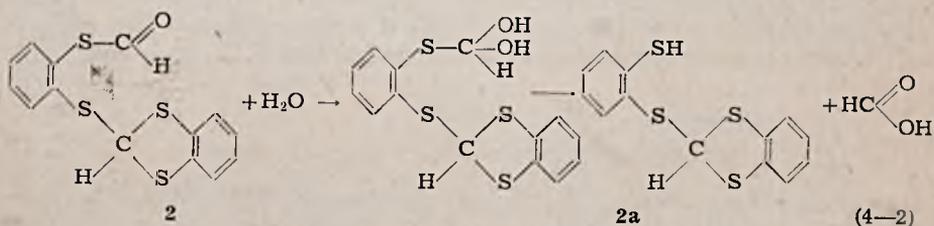
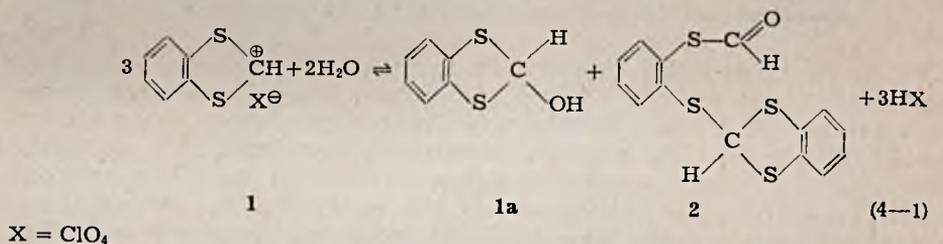
Reaction of salt 1 with water in presence of Et_3N in acetonitrile solution
 Wyniki reakcji soli 1 z wodą w obecności Et_3N w acetonitrylu

Experiment Doświadczenie	H_2O^* mole	Et_3N^* mole	Products (yield, %) (wydajność, %)	
a	15	1.0	4 (20)	2 (40)
b	15	1.05	4 (80)	—
c	47	1.05	4 (60)	—
d	15	1.05	4 (57**)	5 (32**)
e	15	1.05	4 (46**)	5 (43**)

* Mole of reagent per 1 mole of salt 1 — Mole odczynnika na 1 mol soli 1.

** Roughly estimated from NMR data of crude product — Wartości przybliżone, ustalone na podstawie pomiaru widm NMR surowych produktów reakcji.

and amine. No gas evolution was observed in any case. It seems that dithiolium salt 1 undergoes the following reactions under the conditions considered:



Scheme 4

The composition of the reaction mixture after treatment with water is identical with that obtained in acidic hydrolysis (eq. 4—1). Immediately after neutralization there is neither dithiolium salt **1** nor perchloric acid in the solution but thioformate **2** and carbinol base **1a** are still present (see Fig. 9). Then thioformate **2** undergoes hydrolysis with formation of SH group (thiol **2a**, eq. 4—2). This strong nucleophilic reagent reacts readily with carbinol base **1a** yielding *o*-di(benzo-1,3-dithiolythio)benzene (**4**, eq. 4—3). Hydrolysis of **2** is probably the slowest step of the whole process, and it is evidently promoted by traces of amine (compare experiments a with b and c in the Table: in b and c there is a small excess of amine at least at the beginning of hydrolysis).

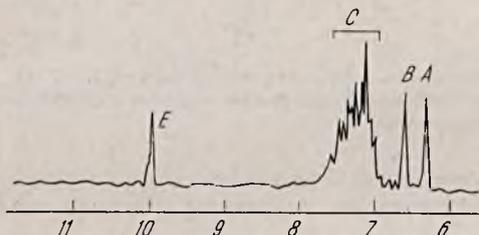
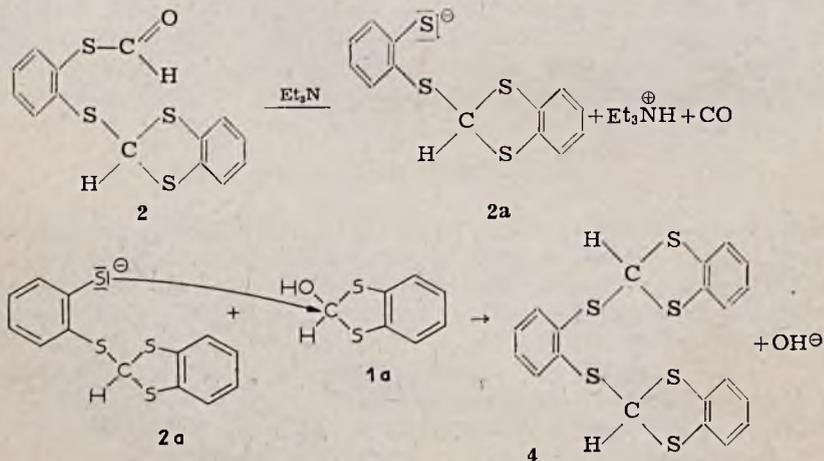


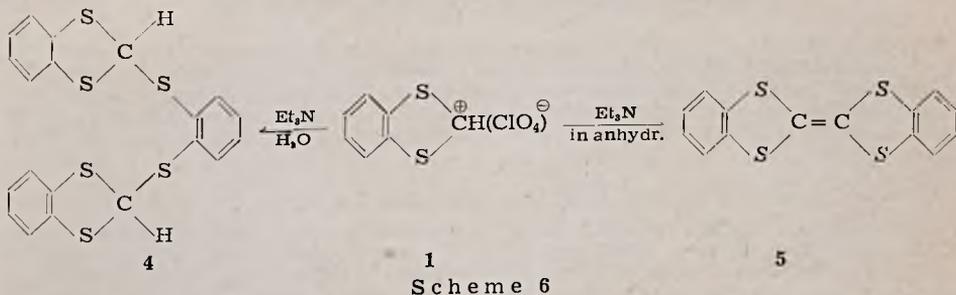
Fig. 9. NMR spectrum of reaction mixture obtained after treatment of benzo-1,3-dithiolium perchlorate (**1**) with water (1.5 mole) and Et_3N (1 mole).

It should be accepted that in a distinctly alkaline solution (using two mole of Et_3N per mole of **1** as in ¹⁾) thiol **2a** is formed as a result of decarbonylation of **2** which is evidently denoted by copious gas evolution during the reaction. The separate experiment (mentioned in ³⁾) consisting in treatment of thioformate **2** (1 mole) with Et_3N (1 mole) in anhydrous conditions followed by addition of salt **1** (1 mole) after gas evolution has ceased and leading to the formation of salt **4** can be also quoted as a further evidence confirming such reaction path (i.e. $2 \rightarrow 2a + \text{CO}$). Taking into account the foregoing considerations we should like to correct the previously ¹⁾ formulated reaction course of salt **1** with water and two mole of Et_3N ; the corrected formulation is given in Scheme 5.



Scheme 5

An interesting observation may be made by comparing the experiments a—c with d—e (Table): the formation of 2,2'-bis(benzo-1,3-dithiolylydene) (5) is observed when salt 1 is treated simultaneously with water and amine. It means that deprotonation of dithiolium ion by Et_3N to the corresponding carbene is realized parallel with the attack of water; the former reaction becomes the only way of reacting in anhydrous conditions (for details see ¹), Scheme 6).



We are carrying analogous experiments with 2-methyl- and 2-phenyl-benzo-1,3-dithiolium salts the results of which will be published.

EXPERIMENTAL

General

Melting points are uncorrected. IR spectra were recorded with UR-10 (Zeiss-Jena) spectrometer. NMR spectra were determined with JNM-C60-HL (Jeol) spectrometer. Chemical shifts (δ) are given in parts per million (ppm) from TMS = 0 as an internal standard. Thin layer chromatography (TLC) was performed on silica Gel G (Merck) using 1:1 or 1:2 benzene—heptane as the solvent mixtures for developing.

Anhydrous acetonitrile was prepared according to ¹. Benzo-1,3-dithiolium perchlorate (1) was obtained as in ¹.

Reactions of salt 1 with water in acidic medium

A (in solution). To a stirred suspension of salt 1 (2.02 g, 0.008 mole) in acetonitrile (15 ccm) or acetone (20 ccm), ca. 5 ccm of water was added until the mixture became homogeneous. The solution was left at room temperature for 15 min, and then treated with water (15 ccm). The separated oil solidified into pink mass when stirred for some time. The product precipitation was completed upon further addition of water (ca. 20 ccm) and stirring for 1 hr. The solid was filtered off, washed with water and dried in vacuum yielding 1.3 g (98%) of crude* *o*-(benzo-1,3-dithiolythio)phenyl thiolformate 2, m.p. 81—84°C (with gas evolution); upon crystallization from benzene—petroleum ether (1:3) with charcoal colourless needles, m.p. 84.5—86°C (with gas evolution). This material becomes pink on the light and must be stored in the dark and cold. IR: 1680 cm^{-1} (C=O). NMR (CH_3CN): 9.98 (s,1), 6.4 (s,1), 7.6—7.1 (m,8).

Analysis:

For $\text{C}_{14}\text{H}_{10}\text{OS}_4$ (322.5) — Calcd.: 52.1% C, 3.3% H, 39.8% S;
found: 52.6% C, 3.5% H, 39.4% S.

* NMR of crude product showed its homogeneity.

B (in heterogeneous system). A suspension of salt **1** (1 g) in water (10 ccm) was shaken 3–4 times with 10 ccm portion of CCl_4 or ether. Combined organic layers were carefully dried over MgSO_4 and evaporated in vacuum to dryness affording colourless crude product, m.p. 79–84° (with gas evolution) in almost quantitative yield. After crystallization from benzene—petroleum ether (1:3) m.p. 84–86°C (with gas evolution) no depression of m.p. with admixture with **2** obtained in A. NMR and IR spectra were identical with those for **2** obtained in A.

Reactions of salt **1** with water in presence of Et_3N

The apparatus for these reactions consisted of a three-necked flask equipped with a mechanical stirrer, a gas-inlet tube reaching over the liquid surface, and a dropping funnel with a pressure equalizing tube and a bubble gauge at the top. The reactions were carried out at room temperature and in argon atmosphere. The set was swept out with argon before use. Standard samples of **4** and **5** were prepared according to¹.

a. with 15 mole of water and 1.0 mole of Et_3N

To a stirred solution of salt **1** (0.5 g, 0.002 mole) in acetonitrile (18 ccm) 0.55 ccm (0.03 mole) of water was added and after 5 min 0.27 ccm (0.002 mole) of Et_3N in acetonitrile (2.5 ccm) was dropped. The reaction mixture was stirred for 3 hrs and left overnight in cold. Colourless crystals which, when separated, afforded *o*-di(benzo-1,3-dithiolylthio)benzene (**4**, m.p. 124–128°C, 0.05 g, 18%; TLC showed its homogeneity and identity with standard sample of **4**). The mother liquors were treated with water (25 ccm) and stirred for 0.5 hr at room temperature to yield 0.12 g of crude thioformate **2** (38%; m.p. 68–75°; TLC showed the presence of some traces of **4**; NMR was almost identical with that of pure **2**).

b. with 15 mole of water and 1.05 mole of Et_3N

To a stirred solution of salt **1** (1.01 g, 0.004 mole) in acetonitrile (28 ccm) 1.1 ccm (0.06 mole) of water was added and after 5 min 0.60 ccm (0.0042 mole) of Et_3N in acetonitrile (2.5 ccm) was dropped. The reaction mixture was stirred for 1 hr, separated colourless crystals were filtered, washed with water and dried in vacuum yielding 0.32 g of *o*-di(benzo-1,3-dithiolylthio)benzene (**4**), m.p. 125–128°C. TLC showed one spot identical with that of standard sample of **4**. The filtrate was poured into water and cooled to give a further portion of product (0.16 g, m.p. 118–123°C; TLC gave the same result as above). The overall yield was 0.48 g (81%); upon crystallization from benzene—heptane (1:4) m.p. 128–130°C. NMR was identical with that of standard sample of **4**.

c. with 47 mole of water and 1.05 mole of Et_3N

To a stirred solution of salt **1** (0.60 g, 0.0024 mole) in acetonitrile (18 ccm) 2 ccm (0.11 mole) of water was added and after 5 min 0.36 ccm (0.0025 mole) of Et_3N in acetonitrile (2 ccm) was dropped. The reaction mixture was stirred for 1 hr, separated colourless crystals were filtered, washed with water and dried in vacuum yielding 0.21 g (60%) of *o*-di(benzo-1,3-dithiolylthio)benzene (**4**, m.p. 122–125°C; TLC gave one spot and was identical with that of standard sample). NMR was the same as above, IR did not show any absorption in C=O region.

d. with 15 mole of water and 1.05 mole of Et_3N (added together)

To a stirred solution of salt **1** (1.01 g, 0.004 mole) in acetonitrile (28 ccm) 1.1 ccm (0.06 mole) of water and 0.60 ccm (0.0042 mole) of Et_3N in acetonitrile (2 ccm) were dropped. The yellow crystals began precipitating immediately. After 45 min of stirring the separate solid was filtered, washed with water and dried in vacuum yielding 0.48 g of product which consisted of bis(benzo-1,3-dithiolylidene-2) (**5**) and *o*-di(benzo-1,3-dithiolylthio)benzene (**4**). TLC of this product gave two spots identical with those of a standard mixture of **4** + **5**. The filtrate was diluted with water (25 ccm), stirred for 1 hr, and left overnight in cold yielding 0.19 g of solid (m.p. 124–141°C) which consisted, according to TLC, of **4** (mainly) and **5** (traces). The pure products were not isolated but their yields were roughly estimated from NMR spectra of crude mixtures to be ca. 57% of **4** and ca. 32% of **5**.

- e. with 15 mole of water and 1.05 mole of Et_3N
(a solution of salt 1 is added)

A solution of salt 1 (1.01 g, 0.004 mole) in acetonitrile (30 ccm) was added to a stirred solution of water (1.1 ccm, 0.006 mole) and Et_3N (0.6 ccm, 0.0042 mole) in acetonitrile (5 ccm). Using strictly the same procedure as above it was obtained: 0.49 g of 4 + 5 mixture, m.p. 158–207°C and 0.18 g of 4 + 5 mixture, m.p. 110–117°C. The yields were estimated as above to be: 46% of 4 and 43% of 5.

o-Di(benzo(1,3-dithiolythio)benzene) 4
(via decarbonylation of 2)

In the same apparatus as above 0.645 g (0.002 mole) of 2 was dissolved in anhydrous acetonitrile (25 ccm) and the set was carefully swept with dry argone. Then 0.28 ccm (0.002 mole) of Et_3N in acetonitrile (5 ccm) was added: a copious gas evolution was observed and a great deal of colourless crystalline solid was precipitated. After 15 min of stirring at room temperature 15 ccm of benzene was added to dissolve the crystals and a solution of salt 1 (0.504 g, 0.002 mole) in acetonitrile (25 ccm) was dropped in. The reaction mixture was left for 1 hr at room temperature and the major part of solvents was then removed in vacuum to yield 0.65 g of 4, m.p. 129–131°C. Further evaporation of filtrate gave 0.15 g of 4, m.p. 126–129°C. The overall yield of 4 was 85%; in TLC it was homogeneous and identical with standard sample of 4. No depression of m.p. on admixture with standard sample of 4 was observed.

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HYDROLIZA NADCHLORANU BENZO-1,3-DITIOLIOWEGO

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Badając podatność na hydrolizę układu benzo-1,3-ditiolu stwierdzono, że w reakcji nadchloranu benzo-1,3-ditioliowego (1) z wodą w środowisku kwaśnym uzyskuje się z bardzo dobrą wydajnością tiolomrówczan *o*-(benzo-1,3-ditiolilolio)fenylu [2,

t.t. 84—86° (z wydzieleniem gazu), IR(KBr): 1680 cm^{-1} , NMR (CH_3CN): 9,98 (s,1), 6,4 (s,1), 7,6—7,1 (m,8)]. Przebieg reakcji powstawania **2**, który nie jest pierwotnym produktem hydrolizy soli **1**, podano w schemacie 1. Pierwszy etap tej reakcji polega na ataku wody na C-2 kationu ditioliowego z wytworzeniem 2-hydroksybenzo-1,3-ditiolu, tzw. zasady karbinolowej **1a**, która w następnym etapie reaguje z solą **1** w wyniku czego powstaje tiolomrówczan **2**, który jest ostatecznym produktem reakcji.

Wprawdzie pierwotny produkt hydrolizy soli **1**, tj. **1a**, nie został wyodrębniony, ale jego obecność w mieszaninie reakcyjnej wykazano na podstawie pomiarów widm NMR roztworów tej soli w CH_3CN , zawierających różne ilości wody (rys. 1—6). Z pomiarów tych wynika, że w badanych roztworach oprócz substratu [sygnały: 11,4 (s,1), 8,8—8,0 (m,4)] i wyodrębnionego produktu [sygnały: 9,98 (s,1), 6,4 (s,1), 7,6—7,1 (m)] istnieje jeszcze drugi produkt hydrolizy, którym prawdopodobnie jest zasada karbinolowa **1a** (sygnały: 6,6 oraz multiplet H_{arom}). Ponadto pomiary te wykazały, że stopień hydrolizy soli ditioliowej rośnie ze wzrostem zawartości wody oraz, że zakwaszenie cofa reakcję (rys. 3—7); jest to więc reakcja odwracalna.

Odwracalność badanej reakcji hydrolizy wykazaliśmy również wykonując pomiary widm NMR roztworów **2** w CH_3CN z dodatkiem wody i kwasu (rys. 7 i 8). Okazało się, że po zakwaszeniu bezwodnego roztworu tiolomrówczanu **2** następuje odtwarzanie się z niego soli ditioliowej, natomiast w obecności wody i kwasu powstaje zasada karbinolowa **1a** (schemat 3). Z omówionych doświadczeń wynika wniosek, że w roztworze soli ditioliowej **1** w obecności H_2O i H^+ ustala się pewien stan równowagi, w którym uczestniczą trzy związki: sól **1**, zasada karbinolowa **1a** oraz tiolomrówczan **2**. Wytrącenie z roztworu tiolomrówczanu **2** powoduje zakłócenie stanu równowagi i w konsekwencji całkowite przereagowanie $1 + 1a \rightarrow 2$. Z tego względu tiolomrówczan **2** jest jedynym produktem uzyskiwanym po reakcji.

Następnie zbadaliśmy reakcje soli **1** polegające na działaniu najpierw wodą, a potem Et_3N w ilościach nieco większej oraz równej molowej ilości soli **1**. Wyniki tej serii doświadczeń podano w tablicy. Okazało się, że w warunkach a—c produktem reakcji jest o-dwu(benzo-1,3-ditiolilotio)benzen (**4**), a więc ten sam związek, który powstaje w przypadku użycia 2 moli aminy na 1 mol soli **1**¹⁾. Przebieg reakcji powstawania związku **2** zależy od ilości użytej aminy; w obecności 2 moli aminy powstający w pierwszym etapie tiolomrówczan **2** ulega dekarbonylacji, o czym świadczy obfite wydzielanie się gazu podczas reakcji, zaś w obecności mniejszych ilości aminy tiolomrówczan **2** ulega hydrolizie (w reakcji nie wydziela się gaz); dalszy bieg reakcji w obu przypadkach jest taki sam, co ilustrują schematy 4 i 5. Potwierdzenie możliwości dekarbonylacji związku **2** uzyskaliśmy w reakcji polegającej na działaniu na ten związek najpierw Et_3N , a następnie—po ustaniu wydzielania się gazu—solą **1**; produktem jej jest związek **4**²⁾.

Ponadto przekonaliśmy się, że jeśli na sól **1** działa się jednocześnie wodą i aminą (dośw. d i e w tablicy), to w reakcji oprócz **4** powstaje również 2,2'-bis(benzo-1,3-ditioliliden) (**5**), co świadczy, że równoległe z atakiem wody, czyli hydrolizą, następuje odprotonowanie soli **1** z wytworzeniem karbenu (schemat 6).