

REACTION OF BENZO-1,3-DITHIOLIUM PERCHLORATE WITH  
SECONDARY ALIPHATIC AMINES

REAKCJA NADCHLORANU BENZO-1,3-DITIOLOWEGO  
Z DRUGORZĘDOWYMI AMINAMI ALIFATYCZNYMI

It is shown by the literature data<sup>1,2)</sup> that 1,3-dithiolium salts of type 1 ( $R_1 = C_6H_5$ ,  $R_2 = H$  or  $C_6H_5$ ,  $X = HSO_4$  or  $ClO_4$ ) react with secondary aliphatic amines to give 2-amino derivatives 2 in very high yields. Pazdro and Polaczkowa<sup>2)</sup> have postulated non-carbenoic course of this reaction suggesting the direct attack of amine on C-2 in 1,3-dithiolium cation.

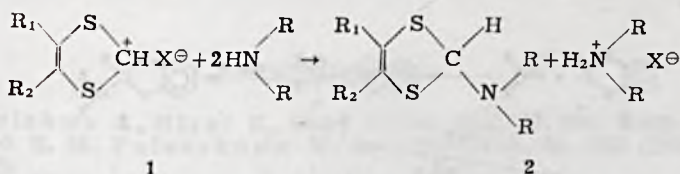
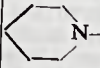
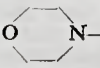
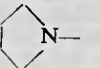


Table — Tablica

Results of reactions of benzo-1,3-dithiolium perchlorate (3) with secondary amines  $\left( \begin{array}{c} R \\ \diagdown \\ N \\ \diagup \\ R \end{array} \right)^a$

Wyniki reakcji nadchloranu benzo-1,3-ditiołowego (3) z drugorzędowymi aminami alifatycznymi

typu  $\begin{array}{c} R \\ \diagdown \\ N \\ \diagup \\ R \end{array}$

Amine	a	b	c	d	e
$\begin{array}{c} R \\ \diagdown \\ N \\ \diagup \\ R \end{array}$		$\begin{array}{c} C_6H_5CH_2 \\ \diagdown \\ N \\ \diagup \\ C_6H_5CH_2 \end{array}$	$\begin{array}{c} (CH_3)_2CH \\ \diagdown \\ N \\ \diagup \\ (CH_3)_2CH \end{array}$		
Yield (%)	2 42b 40b	44c TLC <sup>d</sup>	66c TLC <sup>d</sup>	e 71	e 52

<sup>a</sup> All the reactions were carried out in  $CH_3CN$  solution at room temperature and with molar ratio of amine: salt 3 = 2:1 — Wszystkie reakcje wykonywano w roztworze  $CH_3CN$ , w temperaturze pokojowej, stosując stosunek mowy aminy:soli 3 = 2:1.

<sup>b</sup> Products were chromatographically separated<sup>3)</sup> — Rozdzielenia produktów dokonano metodą chromatografii kolumnowej<sup>3)</sup>.

<sup>c</sup> Satisfactory elemental analyses and supporting spectral data were obtained for 2b and 2a — Dla substancji 2b i 2c uzyskano poprawne wyniki analizy elementarnej oraz zgodne dane widmowe.

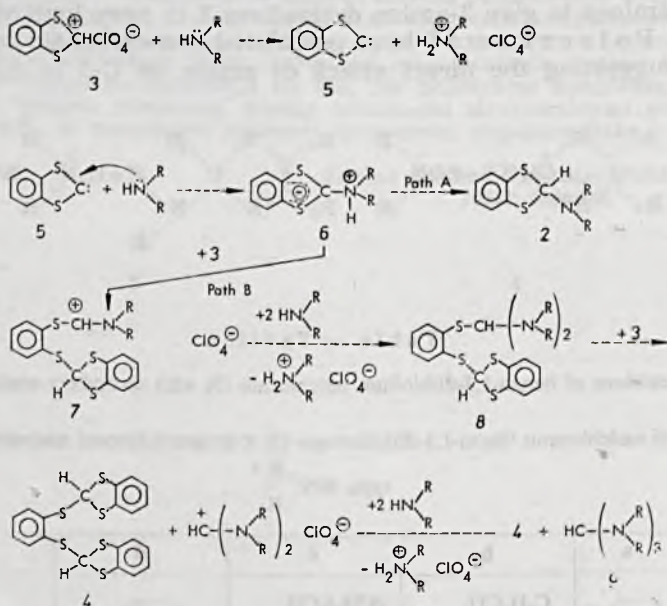
<sup>d</sup> Traces of 4 were detected by TLC but isolation of this product failed — Śladowe ilości związku 4 stwierdzono metodą TLC, jednak próby wydzielenia go metodą chromatograficzną nie dały pozytywnego wyniku.

<sup>e</sup> The isolation of expected 2-amino derivatives (2d and 2e) was attempted by column chromatography but no defined product other than 4 was obtained. In absence of standard samples TLC detection was impossible — Odpowiednie 2-aminozwiązki usiłowano wydzielić metodą chromatografii kolumnowej, ale nie uzyskano żadnego innego produktu oprócz 4. Wobec braku wzorców dla 2d i 2e nie można było wyzyskać TLC do ich wykrywania.

We have found that the reaction of benzo-1,3-dithiolium perchlorate (3) with piperidine (a), dibenzylamine (b) and diisopropylamine (c) afforded two products: corresponding 2-aminobenzo-1,3-dithiole (2a-c;  $R_1, R_2 =$  fused ring) and *o*-di(benzo-1,3-dithiolythio)benzene (4). On the other hand, compound 4 was the main (if not the only) product of reaction when salt 3 was treated with morpholine (d) or pyrrolidine (e). The results of reactions carried out are summarized in the Table.

Compound 4 is known to be very easily formed by the reaction of water on benzo-1,3-dithiolium perchlorate<sup>4)</sup>. Therefore, to exclude the possibility of hydrolysis, all the materials used in the experiments described were carefully dried. Thus, it should be admitted that formation of 4 from salt 3 in this reaction occurs without water participation.

The observed results of the reactions of salt 3 with secondary amines may be explained as follows (Schema).



First, the salt 3 is deprotonated by amine to yield carbene 5 which reacts with the next amine molecule giving the resonance-stabilized ylide 6. Two alternative path-ways of reacting of ylide 6 are possible: A) intramolecular proton-transfer from nitrogen to carbon with formation of 2-amino derivative 2 and B) reaction of ylide 6 with the next molecule of salt 3 involving nucleophilic attack by sulfur on C-2 position of dithiolium cation and resulting in the ring-opening with simultaneous (or followed by) proton-transfer from nitrogen to carbon. Carbonium cation 7 formed in this way reacts immediately with amine to give diamino compound 8 which subsequently affords the final product 4 and triaminomethane (9) according to the Schema.

The non-fused 1,3-dithiolium salts, i.e. 1 ( $R_1 = \text{C}_6\text{H}_5$ ,  $R_2 = \text{H}$  or  $\text{C}_6\text{H}_5$ ,  $\text{X} = \text{HSO}_4$  or  $\text{ClO}_4$ ) react with secondary amines only by path A yielding 2-amino-1,3-dithioles<sup>1,2)</sup>, whereas in the case of benzo-1,3-dithiolium salt

(3) both the reaction paths (A and B) may be parallelly involved or one of them may be predominating. Such a different behavior of salts 1 and 3 towards the same reagent should be related to a greater susceptibility of ring-opening by the fused-ring derivative as compared with non-fused compounds. It should be mentioned that the same conclusion was derived from the experiments concerning the hydrolysis of salts 1 and 3<sup>4,5</sup>.

Other experiments are being carried on. They may permit to explain the above reactions. More detailed report on this problem will be published in *Roczniki Chemii*.

#### Acknowledgment

The authors wish to express their deep gratitude to Wacław Zamłyński, Sc. D., for his encouraging discussion.

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March 18th, 1976.

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#### STRESZCZENIE

W reakcjach nadchloranu benzo-1,3-ditioliowego (3) z piperydyną, dwubenzylaminą i dwuizopropylaminą otrzymano dwa produkty: odpowiedni 2-aminozwiązek (2a—c) oraz o-dwu(benzo-1,3-ditiolilolotio)benzen (4). Związek 4 jest natomiast głównym lub nawet jedynym produktem reakcji soli 3 z morfoliną oraz z piroolidyną (tablica). Dla wyjaśnienia przebiegu tej reakcji przyjęto powstawanie z soli 3 i aminy ylidu 6, który następnie może reagować według drogi A z utworzeniem związku 2, lub według drogi B dając związek 4 (schemat).

Opisane doświadczenia są kolejnym dowodem na to, że układ benzo-1,3-ditiolu cechuje większa tendencja do otwierania pierścienia heterocyklicznego niż układ nie zawierający skondensowanego pierścienia benzenowego<sup>4,5</sup>.

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