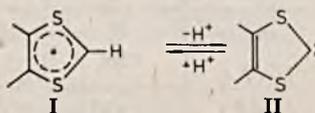


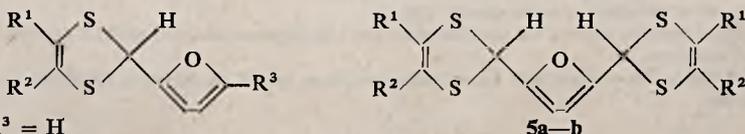
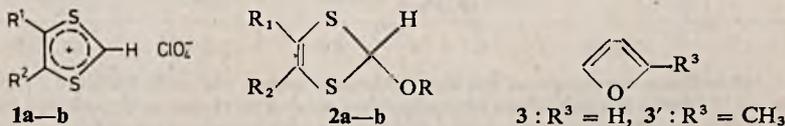
## REACTIONS OF FURAN AND 2-METHYLFURAN WITH 1,3-DITHIOLE DERIVATIVES

The chemistry of 1,3-dithiolium salts (I) and of cyclic carbenes with two  $\alpha$ -sulfur atoms (II) has attracted considerable attention in recent years<sup>1</sup>. The 1,3-dithiolium cation (I) is the conjugate acid of the following dithiacarbene:



The electrophilic character of 1,3-dithiolium salts, which is a result of their molecular structure, has been unambiguously confirmed in a number of reactions with nucleophiles<sup>1a,2,3</sup>. 1,3-Dithiacarbenes II behave as nucleophilic agents in most of the studied reactions<sup>2,4,5</sup> but there are some experimental data<sup>5,6</sup> suggesting that these carbenes may exhibit also electrophilic character, this depending upon the nature of the trapping reagent.

In our experiments we have found that 4,5-diphenyl-1,3-dithiol-2-yl and benzo-1,3-dithiol-2-yl groups may be easily introduced into 2 and (or) 5 positions of furan ring. The following three procedures were used: (A): treatment of furans (3 or 3') with 1,3-dithiolium salt 1a or 1b, (B): treatment of furans (3 or 3') with 2-alkoxy-1,3-dithiol 2a or 2b in presence of trichloroacetic acid, and (C): treatment of furans (3 or 3') with 2-alkoxy-1,3-dithiol 2a or 2b in acetic acid solution.



4a-b :  $R^3 = H$

4'a-b :  $R^3 = CH_3$

a :  $R^1 = R^2 = C_6H_5$ ,  $R = C_2H_5$ ; b :  $R^1, R^2 = -CH=CH-CH=CH-$ ,  $R = CH_3$

The reactions with furan (3) resulted in formation of two products: 2-(1,3-dithiol-2-yl)-furans, 4a or 4b, and 2,5-bis(1,3-dithiol-2-yl)-furans, 5a

or **5b**, respectively. The reactions with 2-methylfuran (**3'**) afforded only one product, i.e. 2-methyl-5-(1,3-dithiol-2-yl)-furans, **4'a** or **4'b**, respectively. The conditions and the results are presented in the Table.

Table

Results of reactions of furans (**3** and **3'**) with 1,3-dithiolium salts (**1a** and **1b**) and with 2-alkoxy-1,3-dithioles (**2a** and **2b**)

Experiment	Reagents	Procedure <sup>a</sup>	Products <sup>b</sup>	M.p. (°C)	Yield (%)
1	<b>1a+3</b>	A	<b>4a</b> <b>5a</b>	57—59 —	62° TLC <sup>d</sup>
2	<b>1a+3'</b>	A	<b>4'a</b>	—	TLC <sup>d</sup>
3	<b>1b+3</b>	A	<b>4b</b> <b>5b</b>	71—73 —	59° TLC <sup>d</sup>
4	<b>1b+3'</b>	A	<b>4'b</b>	—	TLC <sup>d</sup>
5	<b>2a+3</b>	B	<b>4a</b> <b>5a</b>	57—59 —	31° TLC <sup>d</sup>
6	<b>2a+3'</b>	B	<b>4'a</b>	59—61	92
7	<b>2b+3</b>	B	<b>4b</b> <b>5b</b>	71—73 133—136	36° ca. 10°
8	<b>2b+3'</b>	B	<b>4'b</b>	90—93	98
9	<b>2a+3</b>	C	<b>4a</b> <b>5a</b>	57—59 143—144	21° 33°
10	<b>2a+3'</b>	C	<b>4'a</b>	59—61	ca. 100
11	<b>2b+3</b>	C	<b>4b</b> <b>5b</b>	— —	— <sup>d,e</sup> — <sup>d,e</sup>
12	<b>2b+3'</b>	C	<b>4'b</b>	90—93	ca. 100

<sup>a</sup> A: 1,3-Dithiolium salts were refluxed with excess of furans in benzene solution. B: 2-Alkoxy-1,3-dithioles, furans (20 mmole) and Cl<sub>3</sub>CCOOH (0.1 mmole) were refluxed in benzene solution for 15 minutes. C: 2-Alkoxy-1,3-dithioles and furans (1.2 mmole) were allowed to stand in acetic acid solution at room temperature overnight.

<sup>b</sup> Satisfactory elemental analyses and supporting spectral data were obtained for all new compounds.

<sup>c</sup> After separation by column chromatography (SiO<sub>2</sub>).

<sup>d</sup> Pure products were not isolated, but their formation was unambiguously stated by the TLC method. These experiments are still continued.

<sup>e</sup> Benzo-1,3-dithiole (**2b**) was not fully reacted under conditions applied, as shown by NMR and TLC of crude reaction mixtures.

It is noteworthy that the substitution of two 1,3-dithiol-2-yl groups into furan ring takes place even if a great excess of this reagent is used in the reaction (procedure B). This should be attributed to electron-donating effect of cyclic dithioacetal substituent. Furthermore, it seems that 2-methoxy-1,3-benzodithiole (**2b**) is slightly less reactive than 4,5-diphenyl de-

rivative 2a. This may be accounted for by the inductive effect ( $-I$ ) of two phenyl groups.

In the reactions of type A, 1,3-dithiolium cation is undoubtedly the reagent which attacks the furan ring. It is well known that 1,3-dithiolium ions undergo electrophilic substitution with electron-rich aromatic compounds<sup>3</sup>. The course of reaction in cases B and C still remains an open question. It is possible that the furan ring is attacked by 1,3-dithiolium cation formed from 2-alkoxy derivative in presence of an acid, as was suggested by Nakayama<sup>7</sup> in analogous reactions. By analogy with the proposition by Pazdro and Polaczkowa<sup>4</sup>, the cleavage of 2-alkoxy derivatives 2a or 2b into corresponding carbenes may also be assumed. Then the electrophilic substitution of furan ring by 1,3-dithiacarbene would lead to final products. Both above suggestions are very likely and it is rather impossible to draw any definite conclusion regarding the course of these reactions without further investigations.

We are carrying out more detailed experiments along this line. They are going to be published in the *Polish Journal of Chemistry*.

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