

REACTIONS OF 1,3-DITHOLIUM CARBENES *IN SITU* WITH AROMATIC ALDEHYDES

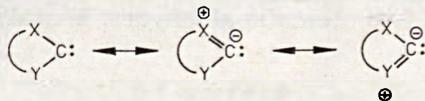
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Stwierdzono, że karbeny 1,3-ditioliowe (3) generowane z różnych pochodnych 1,3-ditiolu reagują z aldehydami aromatycznymi tworząc 2-benzoilo-2,2'-(1',3'-ditiolilo)-1,3-ditiole (6). Zaproponowano i przedyskutowano mechanizm reakcji.

It was found that 1,3-ditholium carbenes (3) generated from various 1,3-dithiole derivatives reacted with aromatic aldehydes to form 2-benzoyl-2,2'-(1',3'-dithioly)-1,3-dithioles (6). The proposed mechanism of reaction has been discussed.

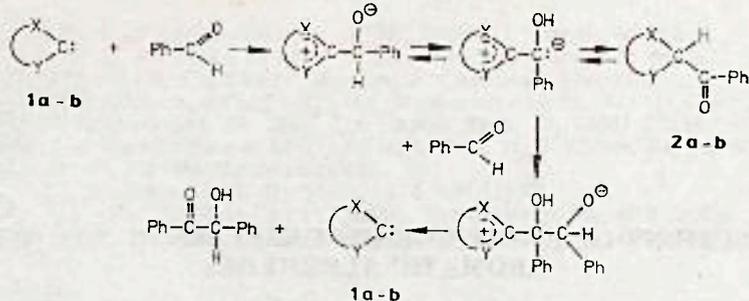
In recent years considerable attention has been focused upon the chemistry of nucleophilic carbenes containing two electron-donating substituents which are usually incorporated into a heterocyclic ring.



Generally, the nucleophilic carbenes are derived from imidazolidine ($\text{X}=\text{Y}=\text{N}-\text{Ph}$), 1,3-thiazole ($\text{X}=\text{S}$, $\text{Y}=\text{N}-\text{R}$) or 1,3-dithiole ($\text{X}=\text{Y}=\text{S}$) systems.

The chemical properties of these carbenes are mainly defined by the lone pair of electrons, but not by the vacant orbital on the carbene carbon atom. The reaction with aromatic aldehydes seems to be particularly interesting among the reactions which reveal the nucleophilic character of such carbenes. It has been stated that some derivatives of 1,3-diphenyl-imidazolidine ¹⁾ and of N-alkyl-1,3-benzothiazole ²⁾, which are believed to be the precursors of carbenes **1**, can catalyze the benzoin condensation of benzaldehyde. Formation of 2-benzoyl derivatives **2**, besides that of benzoin, has been observed in these reactions. Compound **2** is, undoubtedly, formed by carbene **1** insertion into the C—H bond of formyl group. Nucleophilic character of imidazolinium (**1a**) and of thiazolium (**1b**) carbenes has been unquestionably proved by these reactions. Scheme 1 shows the commonly accepted mechanism of this reaction.

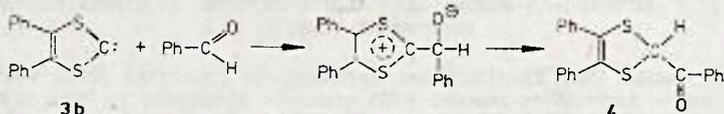
Scheme 1



a: X = N-R, Y = N-R, b: X = N-R, Y = S

Pazdro and Polaczkowa⁸⁾ have reported that 4,5-diphenyl-1,3-dithiolium carbene (**3b**), generated from various 1,3-dithiole derivatives, reacted with benzaldehyde yielding 2-benzoyl-4,5-diphenyl-1,3-dithiole (**4**) according to Scheme 2. Formation of benzoin was not observed.

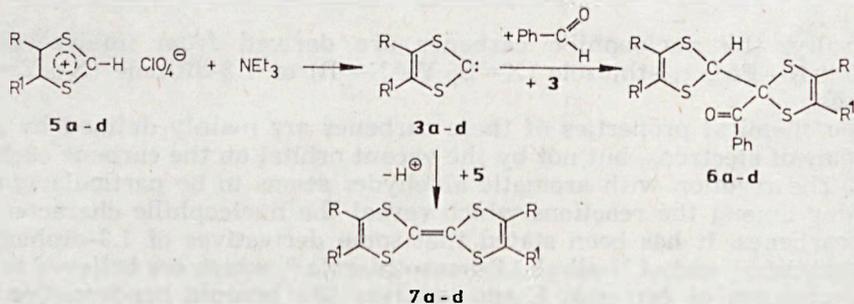
Scheme 2



Formation of product **4** was used by Pazdro and Polaczkowa⁸⁾ as the aldehyde test to indicate the participation of 4,5-diphenyl-1,3-dithiolium carbene (**3b**) in the reactions under investigation.

In our study on reactivity of 1,3-dithiole system we carried out reactions of 4,5-dimethyl-, 4,5-diphenyl-, 4-phenyl-, and benzo-1,3-dithiolium carbenes (**3a-d**) with two aromatic aldehydes: benzaldehyde and *p*-nitrobenzaldehyde.

Scheme 3



a: R = R' = Me, b: R = R' = Ph, c: R = Ph, R' = H,
d: RR' = -CH = CH-CH = CH-

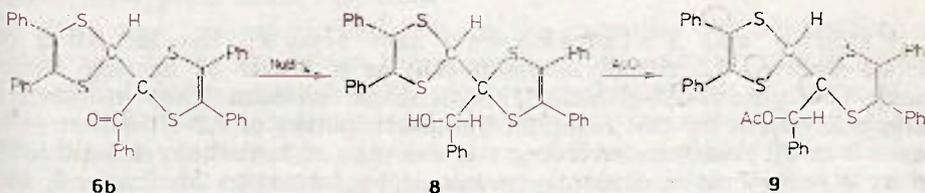
In the first series of experiments respective carbenes were generated from corresponding 1,3-dithiolium perchlorates (**5a-d**) by treatment with triethylamine in presence of a large excess of benzaldehyde (Scheme 3

and Table 1). The main reaction products of all four generated 1,3-dithiolium carbenes **3a—d** with benzaldehyde, including the reaction of 4,5-diphenyl-1,3-dithiolium carbene (**3b**), were 2-benzoyl-2,2'-(1',3'-dithioly)-1,3-dithioles (**6a—d**), but not 2-benzoyl-1,3-dithioles, i.e. compound **4** which would be expected by analogy to Pazdro and Polaczko's statement³). Traces of bis(1,3-dithiolyldienes-2) (**7a—d**), which are dimers of corresponding carbenes, were usually detected in addition to main products **6**, but benzoin was never obtained in these reactions.

According to generally accepted opinion⁴), 1,3-dithiolium salt **5** is deprotonated by the amine molecule to yield carbene **3** which may form dimer **7** with another salt molecule, or may be trapped by the present benzaldehyde affording product **6**. The yield of dimer **7** can be reduced down to traces by using a large excess of benzaldehyde.

The structure of products **6** indicates that the reaction of 1,3-dithiolium carbene with aromatic aldehydes does not involve a simple insertion of the carbene into the C—H bond of formyl group, as suggested by Pazdro and Polaczko³). In our opinion spectral measurements and analytical data (Tables 3 and 4) afforded a proof that these products were correctly represented by formula **6**. However, owing to the disagreement in opinions as to the structure of the reaction product of 4,5-diphenyl-1,3-dithiolium carbene with benzaldehyde, compound **6b** was reduced to carbinal **8** which was then acetylated to acetate **9** (Scheme 4). Results of elemental analysis and spectral data are fully consistent with those formulas that were proposed for compounds **8** and **9**.

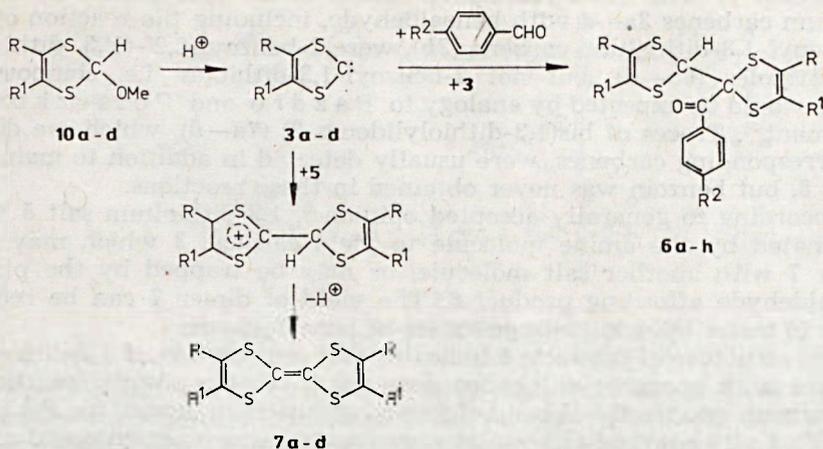
Scheme 4



In the subsequent series of experiments 1,3-dithiolium carbenes **3a—d** were generated from corresponding 2-methoxy-1,3-dithioles **10a—d** in presence of two aromatic aldehydes (benzaldehyde or *p*-nitrobenzaldehyde) by treating **10** with traces of trichloroacetic acid in boiling benzene (procedure of Pazdro and Polaczko⁵) or by treating **10** with glacial acetic acid at room temperature (procedure of Nakayama⁶). Both aldehydes were used in excess as previously. The detailed results of these reactions are collected in Table 2 and illustrated by Scheme 5.

It was found that the main, if not the only, reaction products were 2-benzoyl-2,2'-(1',3'-dithioly)-1,3-dithioles (**6a—d**) or 2-*p*-nitrobenzoyl-2,2'-(1',3'-dithioly)-1,3-dithioles (**6e—h**) when the reaction involved the cleavage of 2-methoxy derivatives **10** catalyzed by trichloroacetic acid in presence of an excess of respective aldehyde. Thus, the products obtained were completely analogous to those formed in the previous series of experiments. In the absence of aldehyde, however, the cleavage of 2-methoxy compounds **10** catalyzed by trichloroacetic acid yielded dimers **7** (Table 2). The tendency of this reaction is clearly related with the structure of substrate **10**.

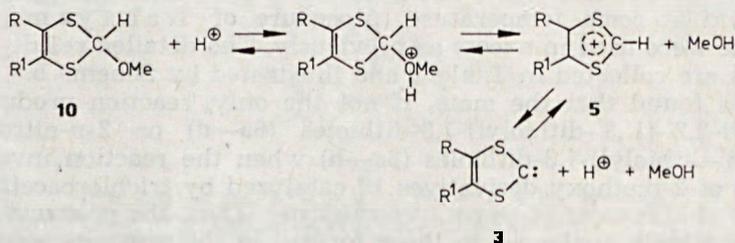
Scheme 5



	R	R ¹	R ²
a	Me	Me	H
b	Ph	Ph	H
c	Ph	H	H
d	—CH = CH—CH = CH—		H
e	Me	Me	NO ₂
f	Ph	Ph	NO ₂
g	Ph	H	NO ₂
h	—CH = CH—CH = CH—		NO ₂

Pazdro and Polaczkowa³⁾ have reported the formation of bis(4,5-diphenyl-1,3-dithiolyli-dene-2) (**7b**) as a result of heating 2-methoxy-4,5-diphenyl-1,3-dithiole (**10b**) in acidic medium. They proposed a carbenic course for this reaction. The participation of 1,3-dithiolium carbenes **3** in all reactions involving the cleavage of 2-methoxy-1,3-dithioles **10** by strong acids is evidently indicated by formation of dimers **7** and compounds **6**. Though the mechanism of the acid-catalyzed cleavage of 2-alkoxy-1,3-dithioles **10** is not known in detail it seems reasonable to assume an equilibrium state between compound **10**, carbene **3** and dithiolium cation **5** in acidic medium (Scheme 6).

Scheme 6



The equilibrium concentrations of 1,3-dithiolium carbene and cation depend on the strength of acid and the basicity of methoxy derivative **10**. They are rather low if a catalytic trace of acid only is added. Under these

conditions the formation of dimers **7** occurs most likely via mechanism of Lemal, involving the reaction of carbene **3** with salt **5** and subsequent deprotonation (Scheme 5). The facility of forming dimers **7** increases with the basicity of methoxy compound **10**. Our experiments have shown that 2-methoxybenzo-1,3-dithiole (**10d**) is a distinctly less reactive compound than all other compounds **10** (Table 2)*.

In the presence of an aldehyde which acts as the trap of carbene **3** equilibrium (**6**) is continuously shifted to the right. The competitive reaction of dimer **7** formation is effectively limited when an appreciable excess of aldehyde is used. As would be expected, the reaction of 1,3-dithiolium carbenes occurs more easily with *p*-nitrobenzaldehyde than with benzaldehyde. 1,3-Dithiolium carbene considered as the most reactive of all is the 4,5-dimethyl derivative, i.e. **3a** (Table 2).

Acetic acid is a less efficient reagent for generation of carbenes **3** from methoxy compounds **10** than trichloroacetic acid (Table 2). The benzo derivative **10d**, which is the least reactive of all under consideration, has not been practically attacked in acetic acid medium. Furthermore, the selectivity of reaction is so diminished that formation of dimers **7** along with derivatives **6** is almost always observed under these conditions even when a large excess of aldehyde is used.

From the results of the second series of our experiments we conclude that the yield of benzoyl derivatives **6** depends on: (i) the structure of methoxy compound **10**, (ii) the strength of acid used, (iii) the nucleophilic character of generated carbene **3**, and (iv) the electrophilic character of aldehyde applied in the reactions.

Two very interesting remarks upon the chemistry of 1,3-dithiolium system may be deduced from the analysis of our experiments: (i) Though 1,3-dithiolium carbenes **3** undoubtedly reveal nucleophilic properties in the reactions with aromatic aldehydes, nevertheless they do not catalyze the benzoin condensation; (ii) Reactions of these carbenes with aldehyde do not lead to 2-benzoyl-1,3-dithioles which would be expected in consequence of a simple insertion of carbene into the C—H bond of formyl group. The reaction products are composed of two 1,3-dithiole rings and one benzoyl group in the molecule and their structure is represented by formula **6**. Both these observations clearly point to the essentially different behavior of 1,3-dithiolium carbenes in comparison with that of thiazolium and imidazolinium.

The following pathways of formation of compounds **6** from 1,3-dithiolium carbenes and aldehyde can be suggested (Scheme 7). Of course, the now available data are rather insufficient to consider the mechanism of this reaction as fully explained. Nucleophilic attack of carbene **3** on carbonyl carbon atom in aldehyde yields the zwitterionic adduct **A** which subsequently can react in the following ways:

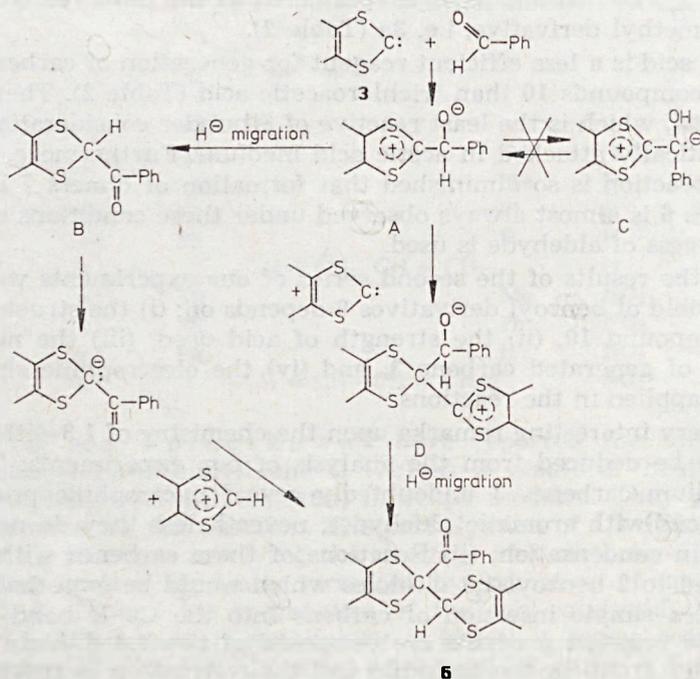
(i) Migration of the proton from the carbonyl carbon atom to oxygen gives an ylide intermediate **C** (**A** → **C**). Such rearrangement is generally postulated in the reactions of thiazolium and imidazolinium carbenes with

* A more detailed report on this problem will be published in *Polish Journal of Chemistry*.

aldehydes and these ylide intermediates are considered to be the proper catalyst of benzoin condensation¹⁻²⁾ (cf. Scheme 1). We suppose that adjacent 1,3-dithiolium ring does not favor the formation of such ylide structure and for this reason 1,3-dithiolium carbenes do not catalyze the benzoin condensation. Thus, the conversion $A \rightarrow C$ may be ignored.

(ii) Migration of hydride ion from the carbonyl carbon atom to the C-2 of dithiolium ring affords 2-benzoyl-1,3-dithiole ($A \rightarrow B$). This way of reaction was suggested by Pazdro and Polaczkowa³⁾ who have incorrectly recognized the structure of the product obtained.

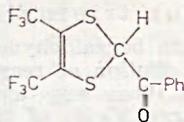
Scheme 7



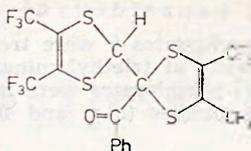
(iii) Attack of zwitterionic adduct **A** by another 1,3-dithiolium carbene to yield the intermediate **D** which subsequently undergoes the hydride shift to the final product, i.e. compound **6** ($A \rightarrow D \rightarrow 6$).

It seems conceivable that the final product **6** could be formed from 2-benzoyl-1,3-dithiole (**B**) according to Scheme 7 ($B \rightarrow 6$). However, we prefer the sequence $A \rightarrow D \rightarrow 6$ as the main pathway of the reaction of 1,3-dithiolium carbenes with aromatic aldehydes, because formation of compound **B** was never observed in our experiments.

Hartzler⁷⁾ in his short communication has described the formation of compound **12** the structure of which is analogous with that of benzoyl derivative **6**. In this paper compounds **11** and **12** are mentioned as the products of reactions involving the generation of 4,5-di(trifluoromethyl)-1,3-dithiolium carbenes by thermal reaction of carbon disulfide with hexafluor-2-butyne in presence of benzaldehyde.



11



12

Unfortunately the data cited in this paper are insufficient to compare these results with ours.

EXPERIMENTAL

^1H NMR and ^{13}C NMR spectra were determined on Jeol JNM MN100 and Varian CFT-20 spectrometer, respectively, using TMS ($\delta = 0$ ppm) as internal standard. IR spectra were recorded on Specord 71 IR spectrometer. Mass spectra were taken on LKB 2091 spectrometer with an ionizing voltage 15 eV and 70 eV. All melting points were uncorrected. Acetonitrile and acetic acid used were refluxed over and distilled from phosphorus pentoxide. Acetonitrile was stored over molecular sieves. Triethylamine was refluxed over, distilled from and then stored over potassium hydroxide. Benzaldehyde was distilled prior to use.

Starting materials *

4,5-Dimethyl-1,3-dithiolium perchlorate (**5a**, m.p. 118–120°C) and 2-methoxy-4,5-dimethyl-1,3-dithiole (**6a**, b.p. 70°C/1 Torr) were prepared by the method which has not yet been published⁹).

4,5-Diphenyl-1,3-dithiolium perchlorate (**5b**, m.p. 186–187°C (decomp.), lit.⁹): 181°C) and 4-phenyl-1,3-dithiolium perchlorate (**5c**, m.p. 182–183°C (decomp.), lit.⁹): 179–180°C (decomp.)) were prepared by a modified procedure described in⁹).

Benzo-1,3-dithiolium perchlorate (**5d**, m.p. 186–187°C (decomp.), lit.¹⁰): 185°C (decomp.) was prepared by analogy to¹¹).

2-Methoxy-4,5-diphenyl-1,3-dithiole (**6b**, m.p. 75–76°C, lit.⁹): 78°C) was prepared according to⁹). 2-Methoxy-4-phenyl-1,3-dithiole (**6c**, m.p. 57–58°C, lit.¹²): 61°C) was prepared according to¹²). 2-Methoxybenzo-1,3-dithiole (**6d**, m.p. 36–37°C, lit.¹³): oil solidified in a refrigerator) was prepared according to¹³).

Reactions of 1,3-dithiolium perchlorates 5

(a) With triethylamine in presence of benzaldehyde

A solution of 1 mmole of perchlorate **5** in 7.5 ccm of acetonitrile was slowly dropped (for ca. 0.5 hr) to stirred solution of 100 mmole of benzaldehyde and 1 mmole of triethylamine in 5 ccm of acetonitrile. The reaction mixture was stirred for 0.5 hr at room temperature and then diluted with ca. 100 ccm of ethyl ether. The ethereal sulfide for 1 hr. The precipitated solid was filtered off. Organic layer was washed with water, aqueous solution of sodium hydrogen carbonate and water. After drying over MgSO_4 , the solvent was evaporated in vacuum. The composition of crude product was tested by TLC and then treated with methanol to precipitation. The products were purified by crystallization and analyzed. The relevant results are presented in Tables 1, 3 and 4.

* Detailed report on the synthesis of 2-methoxy-1,3-dithioles (**6a–d**) and 1,3-dithiolium perchlorates (**5a–d**) will be published in the *Polish Journal of Chemistry*.

(b) With benzaldehyde without triethylamine

1,3-Dithiolium perchlorates **5** were treated with benzaldehyde in the same way as above but in absence of triethylamine. After dilution of reaction mixture with ethyl ether the initial perchlorates were recovered. They were identified by comparison with standard samples (m.p. and IR spectra). Yields of recovered salts are listed in Table 1.

Table 1
Products and yields of reactions of 1,3-dithiolium perchlorates
5a—d

Salt	Reaction with Et ₃ N and BzH		Reaction with BzH without Et ₃ N
	Products ^a	Yield %	Recovered salt 5 %
5a	6a 7a^b	68	91
5b	6b 7b^b	93	87
5c	6c 7c^b	80	89
5d	6d 7d^b	62	88

^a Physical, analytical and spectral data for compounds **6a—d** are presented in Tables 3 and 4.

^b Traces detectable by TLC only.

Reactions of 2-methoxy-1,3-dithioles **10**

(a) With trichloroacetic acid in presence of aldehydes

A solution of 0.1 mmole of trichloroacetic acid in 1 ccm of benzene was rapidly added to a boiling solution of 1 mmole of **10** and 20 mmole of aldehyde in 7 ccm of benzene. The solution was refluxed for 15 min. After cooling the reaction mixture was passed through a column with silica gel. This operation was omitted in the reactions with *p*-nitrobenzaldehyde. The aldehyde excess was removed by treating with sodium bisulfite, as described previously. The crude residue was analyzed and then purified by crystallization. Respective results are presented in Tables 2, 3 and 4.

(b) With benzaldehyde without trichloroacetic acid

Compounds **10** were treated with benzaldehyde without addition of trichloroacetic acid in the same manner as above. In all cases unchanged substrates **10** were recovered with almost quantitative yields (¹H NMR spectra).

(c) With trichloroacetic acid without aldehyde

A solution of 0.1 mmole of trichloroacetic acid in 1 ccm of benzene was rapidly added to a boiling solution of 1 mmole of **10** in 7 ccm of benzene. Reflux was continued for 1 hr, whereas in the case of **10a** for 15 min. After cooling, the reaction mixture was passed through a column with silica gel and analyzed by TLC. The solvent was evaporated, 10 ccm of methanol was added to the crude residue and refluxed. The precipitated dimers **7** were filtered off, washed with methanol and identified by comparison with standard samples (m.p. and TLC). Yields of products are listed in Table 2.

Table 2
Products and yields of reactions of 2-methoxy-1,3-dithioles 10a-d^a

Me- thoxy com- pound	Reactions with CCl ₃ COOH														
	and BzH			and <i>p</i> -NO ₂ BzH			without aldehyde			and BzH			and <i>p</i> -NO ₂ BzH		
	Products	Yield %		Products	Yield %		Products	Yield %	M.P. °C	Products	Yield %		Products	Yield %	
10a	6a	ca. 100		6e	ca. 100		7a (10a)	76 TLC	240—243 ^(c)	(6a) 7a	15 ^b		6e (7a)	68 ^b	
10b	6b	ca. 100		6f	ca. 100		7b	71	262—263 ^(c)	6b (7b) (10b)	75 ^b TLC		(6f) (7b) (10b)	85 ^c TLC 15 ^b	
10c	(6c) (10c)	80 ^c 20 ^c		6g	ca. 100		7c	34	196—198 ^(c)	(6c) (7c) (10c)	74 ^c TLC 26 ^c		6c (7c) (10c)	79 ^b TLC TLC	
10d	6d (10d)	10 ^b		6h (7d) (10d)	53 ^c TLC		(7d) (10d)	TLC		(10d)			(10d)		

^a Products in parentheses were not isolated; they were stated by ¹H NMR spectra of reaction mixtures.

^b Products precipitated from reaction mixture; the residue was not separated.

^c Calculated from ¹H NMR spectrum of reaction mixture. TLC.—Formed in trans detectable by TLC only.

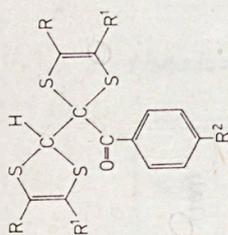


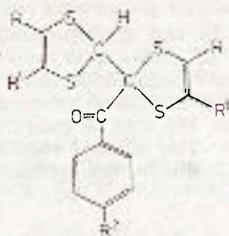
Table 3

Synthetic and analytical data of 2-benzoyl-2,2-(1,3-dithioly)-1,3-dithioles 6a-h

Compound No	R	R'	R ²	M.p. °C	Crystallized from	Formula	Analysis, %											
							Calculated						Found					
							C	H	S	N	C	H	S	N				
6a	Me	Me	H	136—138	MeOH	C ₁₇ H ₁₈ S ₄ O	55.7	4.9	35.0	—	—	55.8	4.9	34.3	—			
6b	Ph	Ph	H	186—188 (decomp.)	CCl ₄	C ₃₇ H ₂₆ S ₄ O	72.3	4.2	20.9	—	—	72.3	4.3	20.1	—			
6c	PH	H	H	130—133 (decomp.)	MeOH	C ₂₅ H ₁₈ S ₄ O	64.9	3.9	27.7	—	—	64.9	3.9	27.5	—			
6d	—CH=CH—	CH=CH—	H	180—182 (decomp.)	MeOH	C ₂₁ H ₁₄ S ₄ O	61.5	3.4	31.2	—	—	61.2	3.6	31.9	—			
6e	Me	Me	NO ₂	139—142	AcOH	C ₁₇ H ₁₇ S ₄ NO ₃	49.6	4.1	31.1	3.4	3.4	49.7	4.1	30.8	3.3			
6f	Ph	Ph	NO ₂	138—140	Et ₂ O—petr. ether 1:5	C ₃₇ H ₂₅ S ₄ NO ₃	67.4	3.8	19.4	2.1	2.1	67.4	4.1	19.5	2.0			
6g	Ph	H	NO ₂	155—156	AcOH	C ₂₅ H ₁₇ S ₄ NO ₃	59.2	3.4	25.3	2.8	2.8	59.1	3.3	25.6	2.7			
6h	—CH=CH—	CH=CH—	NO ₂	180—182	MeOH	C ₂₁ H ₁₃ S ₄ NO ₃	55.4	2.9	28.1	3.1	3.1	55.0	3.0	27.7	2.7			

Table 4

Spectral data of 2-benzoyl-2,2'-(1',3'-dithiolyloxy)-1,3-dithioles 6a-h



Compound No	R	R ¹	R ²	¹ H NMR		IR in CCl ₄ ν, cm ⁻¹	MS M ⁺ , m/e
				δ, ppm	solvent		
6a	Me	Me	H	1.65 (s, 6H), 1.83 (s, 6H), 5.24 (s, 1H), 7.26–7.40 (m, 3H), 8.0–8.12 (m, 2H)	CCl ₄	1675 (C=O)	366
6b ^a	Ph	Ph	H	5.55 (s, 1H), 7.02 (s, 10H), 7.11 (s, 10H), 7.35–7.45 (m, 3H), 8.27–8.41 (m, 2H)	CCl ₄	1673 (C=O)	614
6c	Ph	H	H	5.77 (s, 1H), 6.07 (s, 1H), 6.19 (s, 1H), 7.05–7.38 (m, 13H), 8.13–8.25 (m, 2H)	CCl ₄	1673 (C=O)	462
6d	-CH=CH-CH=CH-		H	5.74 (s, 1H), 6.87 (s, 4H), 6.99 (s, 4H), 7.23–7.36 (m, 3H), 7.99–8.12 (m, 2H)	CCl ₄	1675 (C=O)	410
6e	Me	Me	NO ₂	1.71 (s, 6H), 1.84 (s, 6H), 5.24 (s, 1H), 8.19 (s, 4H)	CCl ₄	1685 (C=O) 1535 (NO ₂) 1350	
6f	Ph	Ph	NO ₂	5.52 (s, 1H), 7.03 (s, 10H), 7.12 (s, 10H), 8.16–8.53 (q, 4H)	CCl ₄	1683 (C=O) 1533 (NO ₂) 1350	
6g ^b	Ph	H	NO ₂	5.80 (s, 1H), 6.13 (s, 1H), 6.23 (s, 1H), 7.22–7.34 (m, 10H), 8.15–8.39 (q, 4H)	CDCl ₃	1657 (C=O) 1515 (NO ₂) 1340	
6h ^b	-CH=CH-CH=CH-		NO ₂	5.75 (s, 1H), 6.95 (s, 4H), 7.05 (s, 4H), 8.13 (s, 4H)	CDCl ₃	1675 (C=O) 1525 (NO ₂) 1345	

^a ¹³C NMR (CDCl₃), δ (SOFR): C-2' = 58.89(d), C-2 = 76.15(s), C=O = 194.27 (s).

^b IR in KBr pellets.

(d) Cleavage of 2-methoxy-1,3-dithioles 10
in acetic acid in presence of aldehydes

A solution of 1.25 mmole of 10 and 25 mmole of benzaldehyde (or 1.5 mmole of *p*-nitrobenzaldehyde) in 3.8 ccm of acetic acid was allowed to stand for 24 hrs at room temperature. If any crystals separated, they were filtered off, washed with acetic acid and methanol, dried and analyzed by spectral methods. The filtrate or the reaction mixture was diluted with 100 ccm of ethyl ether and washed with water to a neutral reaction of water layer. The ethereal solution was worked up as described in point a of the reactions of 1,3-dithiolium perchlorates. The results are listed in Tables 2, 3 and 4.

2-Hydroxybenzyl-2,2'-(4',5'-diphenyl-1'-3'-dithioly)-4,5-diphenyl-1,3-dithiole (8)

To a stirred solution of 1 mmole of 6b in 35 ccm of 1,2-dimethoxyethane 1 mmole of sodium borohydride was added slowly. After stirring for 0.5 hr at room temperature the solvent was removed in vacuum, 50 ccm of water was added to the residue and the mixture was left overnight in a refrigerator. Crude product was filtered off, washed with water and dried. The yield was ca. 100%, m.p. after crystallization from ethanol 160–161°C.

¹H NMR (CCl₄), δ: 2.94 (d, 1H), 5.04 (s, 1H), 5.20 (d, 1H), 6.88–7.66 (m, 20H); ¹³C NMR (CDCl₃), δ (SOFR): C-2' = 58.33 (d), C-OH = 74.35 (d), C-2 = 82.45 (s); IR (CCl₄), ν: 3500 and 3600 cm⁻¹ (OH); MS, *m/e*: 616 (M⁺).

Analysis:

For C₃₇H₂₃S₄O — Calcd.: 72.1% C, 4.6% H, 20.8% S;
found: 71.9% C, 4.8% H, 19.9% S.

2-Acetoxybenzyl-2,2'-(4',5'-diphenyl-1',3'-dithioly)-4,5-diphenyl-1,3-dithiole (9)

To a solution of 0.25 mmole of 8 in 0.25 ccm of pyridine there was added 0.025 ccm of acetic chloride and heated to 60°C. After cooling 20 ccm of water was added and the reaction mixture was left for ca. 3 hrs. Crude product was filtered off, washed with water and dried. Yield ca. 100%, m.p. after crystallization from methanol 173–176°C.

¹H NMR (CCl₄), δ: 2.00 (s, 3H), 5.12 (s, 1H), 6.40 (s, 1H), 6.90–7.35 (m, 23H), 7.59–7.74 (m, 2H). IR (CCl₄), ν: 1760 cm⁻¹ (C=O).

Analysis:

For C₃₉H₃₀S₄O₂ — Calcd.: 71.1% C, 4.6% H, 19.5% S;
found: 70.8% C, 4.7% H, 18.9% S.

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