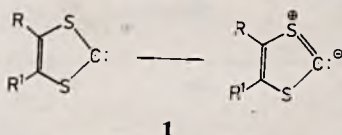


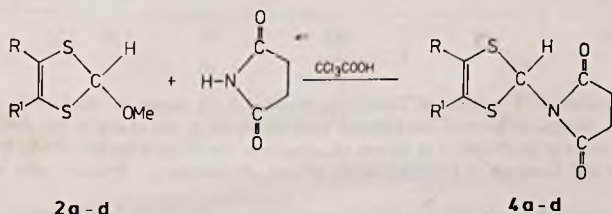
REACTIONS OF 1,3-DITHIOLIUM CARBENES *IN SITU* WITH N—H ACID COMPOUNDS

The chemistry of 1,3-dithiole and, particularly, the reactivity of 1,3-dithiolium carbenes **1**, has recently attracted considerable attention. The nucleophilic character of carbenes **1**, which is the result of their molecular structure, has been unambiguously confirmed in reactions with 1,3-



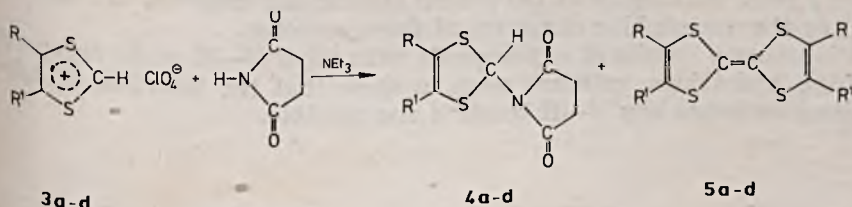
dithiolium salts ¹⁾, C—H acidic compounds ²⁾ and aromatic aldehydes ^{3,4)}.

In our experiments we have found that 1,3-dithiolium carbenes **1**, generated *in situ*, were trapped by succinimide used in suitably large excess to yield products of insertion into the N—H bond of imide. Carbenes **1** were generated in two ways: (A): from 2-methoxy-1,3-dithioles **2a—d** by treatment with trace of trichloroacetic acid ^{2,4)}, (B): from 1,3-dithiolium perchlorates **3a—d** by treatment with triethylamine ⁴⁾. 2-Succinimido-1,3-dithioles **4a—d** were the only reaction products, when carbenes were generated according to procedure A.



a : R = R' = Me, **b** : R = R' = Ph, **c** : R = Ph, R' = H,
d : RR' = —CH = CH—CH = CH—.

However, when carbenes **1** were generated according to procedure B, then in addition to **4a—d**, the formation of bis(1,3-dithiolyldenes-2) **5a—d**, i.e. dimers of corresponding carbenes, was observed.



3a—d

4a—d

5a—d

4a—d as above.

The conditions and results of these reactions are presented in the Table.

Table

Results of reactions of succinimide with 2-methoxy-1,3-dithioles **2a—d** and with 1,3-dithiolium perchlorates **3a—d**

No	Precursor of carbene	Procedure ^a	Products ^b	Yield %	M.p. ^c °C	Time of reaction hr
1	2a	A	4a	98	142—144 decomp.	0.5
2	2b	A	4b	96	185—190 decomp.	1.5
3	2c	A	4c	96	122—124 decomp.	2.0
4	2d	A	4d	98	155—158	4.5
5	3a	B	4a 5a	80 19	130—135 ^d decomp.	—
6	3b	B	4b 5b	45 52	174—180 ^d decomp.	—
7	3c	B	4c 5c	52 46	119—120 ^d decomp.	—
8	3d	B	4d 5d	65 34	150—155 ^d	—

^a A—A suspension of 1 mmole of 2-methoxycompound **2**, 20 mmole of succinimide and 0.1 mmole of trichloroacetic acid in 30 ccm of benzene was refluxed until compound **2** was absent in the reaction mixture (TLC).
^b B—A solution of 1 mmole of perchlorate **3** in 10 ccm of acetonitrile was dropped for ca. 0.5 hr into a solution of 50 mmole of succinimide and 1 mmole of triethylamine in 50 ccm of acetonitrile. Products were separated by column chromatography.

^b Satisfactory elemental analyses and supporting spectral data were obtained for all new compounds (**4a—d**).

^c Melting points are given only for new compounds (**4a—d**).

^d Melting point of crude product obtained after column chromatography.

We have stated in independent experiments that either 2-methoxy compounds **2a—d** (without acid) or perchlorates **3a—d** (without amine) did not react with succinimide. Therefore, we suppose that 1,3-dithiolium carbenes **1** react with imide as the proton abstracting reagents, this again indicating the nucleophilic character of these carbenes.

Preliminary results of experiments with other N—H acidic compounds (amides, hydrazides, anilides) seem to show that the insertion of 1,3-dithiolium carbenes into N—H bonds is also possible.

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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