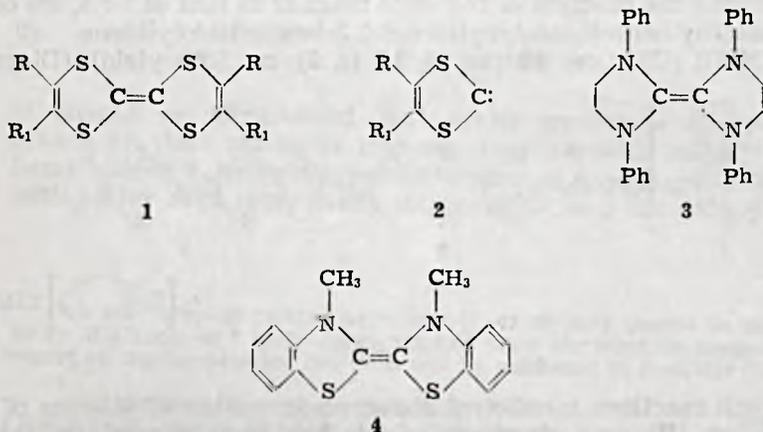


SYNTHESIS OF UNSYMMETRICALLY SUBSTITUTED "ELECTRON-RICH" OLEFINES

SYNTEZA NIESYMETRYCZNIE PODSTAWIONYCH OLEFIN
„BOGATYCH W ELEKTRONY”

The bis (1,3-dithiolylidene-2) system (1) may be formally considered as a dimer of carbene 2, analogically to typical dimers of nucleophilic carbenes such as 3 or 4:



1A: $R=R_1=Ph$

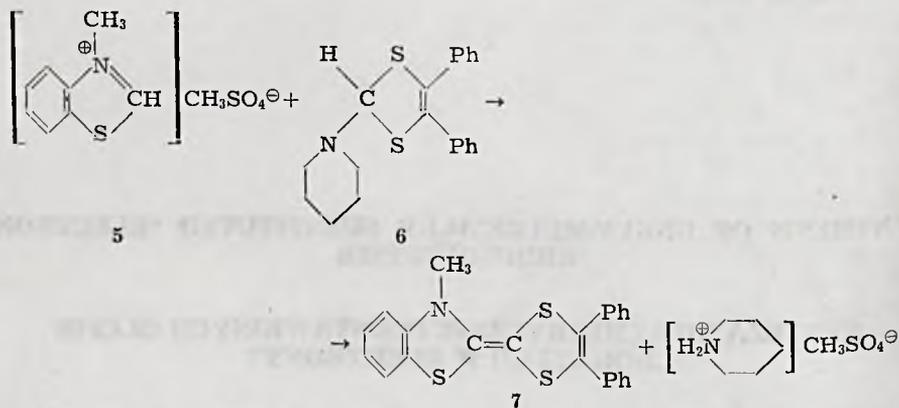
1B: $R/R_1=-CH=CH-CH=CH-$

However, contrary to dimers 3 and 4, which are more or less reactive towards electrophilic reagents ($3 > 4$)¹⁻³, dithiolylidene dimer proved to be completely passive towards electrophiles and did not display properties of a nucleophilic carbene. This has been confirmed for two compounds (1A and 1B) in our laboratory⁴.

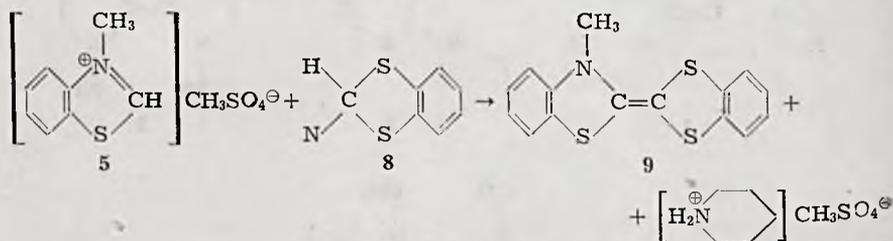
For that reason we got interested in the unsymmetrical alkene of

the type $\begin{matrix} -S & & S- \\ & \diagdown & / \\ & C=C & \\ & / & \diagdown \\ =N & & S- \end{matrix}$, in its stability and reactivity.

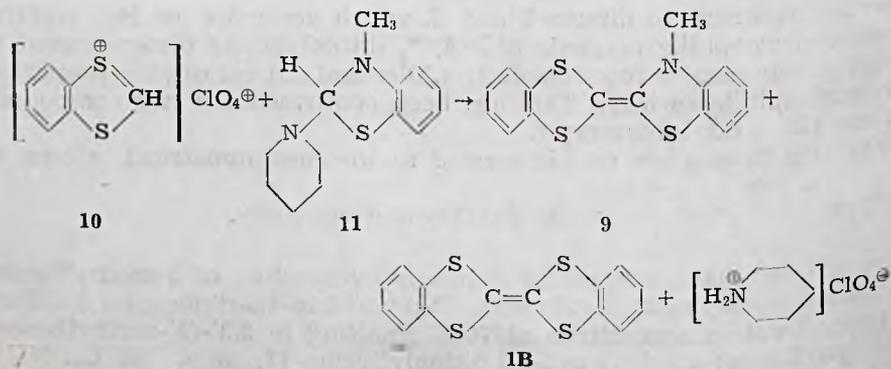
Therefore, we accomplished its synthesis by reaction of 3-methylbenzothiazolium methylsulfate (5) with 2-piperidine-4,5-diphenyl-1,3-dithiol (6) carried out in acetonitrile at 70°C resulting in 2,2'-(3'-methylbenzothiazolynylidene)-4,5-diphenyl-1,3-dithiolylidene (7; m.p. 163°C, NMR (CS₂): 6.52—7.05 (m, 14), 4.45 (s, 3); 75% yield). (Diagram 1).



Starting from thiazolium salt **5** and 2-piperidinebenzo-1,3-dithiol (**8**; m.p. 87°C; NMR (CCl₄): 6.85—6.97 (m, 4), 6.0 (s, 1), 2.45 (m, 4), 1.45 (m, 6)) and carrying the reaction in the same manner as that of **5** + **6**, we obtained 2,2'-(3'-methylbenzothiazolynylidene)-1,3-benzodithiolylidene (**9**; m.p. 179°C; NMR (CS₂): ca. 6.9 (m, 8), 3.5 (s, 3); ca. 50% yield). (Diagram 2):



In both reactions mentioned above no formation of alkenes of type **1** (i.e. **1A** or **1B**) was observed, which has been proved by thin-layer chromatography. On the other hand, the reaction of benzo-1,3-dithiolium perchlorate (**10**) with 2-piperidine-3-methylbenzothiazoline (**11**) (Diagram 3) led to the formation of **1B** in addition to the expected compound **9**.



We are now carrying some experiments which may lead to more accurate informations concerning the course of reactions of 2-piperidine derivatives **6**, **8** and **11** with olium salts.

Unsymmetrical alkenes **7** and **9** are stable in crystalline form, but their solutions undergo gradual decomposition during storage.

Compound **7** when heated with sulfur in pyridine (5 hrs, at about 100°C) yielded a mixture of 4,5-diphenyl-1,3-dithiolylthione-2 (**12**) and 3-methylbenzothiazolthione-2 (**13**) (Diagram 4). Thione **12** was separated in an almost quantitative yield. The presence of thione **13** in the post-reaction mixture has only been demonstrated chromatographically (by comparison with a standard chromatogram), but its separation in pure state has not yet been successful.

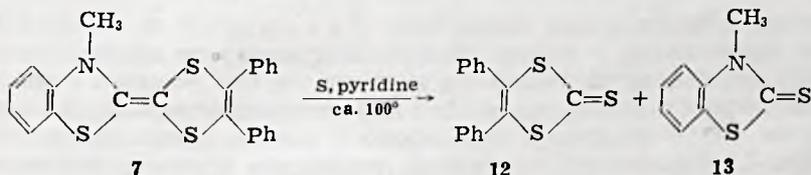


Diagram 4

It should be emphasized that under conditions applied (Diagram 4) alkane **1A** does not enter into any reaction with sulfur⁴. On the other hand, alkene **4**, being a typical example of a nucleophilic carbene, reacts with sulfur even more easily (temp. 50°C; in 2 hrs 64% yield⁸).

We are carrying further experiments which may permit to establish the reactivity of alkenes of **7** and **9** types towards other electrophilic reagents. More detailed report on the investigated reactions will be published in *Roczniki Chemii*.

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STRESZCZENIE

W reakcji metylosiarczanu 3-metylobenzotiazoliowego (**5**) z 2-piperidyno-4,5-dwufenyl-1,3-ditiolem (**6**), prowadzonej w acetonitrylu w temp. 70°, otrzymano 2,2'-(3'-metylobenzotiazolinylideno)-4,5-dwufenyl-1,3-ditoliliden (**7**; t.t. 163°; NMR (CS₂): 6,52—7,05 (m, 14), 3,45 (s, 3); wyd. 75%). W takich samych warunkach z **5** i 2-pi-

perydyno-benzo-1,3-ditiolu (8) otrzymano 2,2'-(3'-metylobenzotiazolinylideno)-benzo-1,3-ditioliliden (9; t.t. 179°; NMR (CS₂): ok. 6,9 (m, 8), 3,5 (s, 3); wyd. ok. 50%). W obu reakcjach nie zaobserwowano powstawania symetrycznie podstawionych alkenów typu 1.

Biorąc do reakcji nadchloran benzo-1,3-ditioliowy (10) i 2-piperydyno-3-metylobenzotiazolinę (11) otrzymano mieszaninę dwóch produktów: 9 i 1B (schemat 3).

Obecnie prowadzone są badania mające na celu wyjaśnienie przebiegu reakcji pochodnych 2-piperydynowych z solami oliowymi.

Alken 7 ogrzewany 5 godz. do temp. 100° z siarką w pirydyynie przereagował zgodnie ze schematem 4. Należy podkreślić, że alkeny 1A i 1B nie ulegają reakcji z siarką w tych warunkach⁴⁾, zaś alken 4 reaguje z siarką nawet w warunkach łagodniejszych⁵⁾.

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