

SYNTHESIS OF UNSYMMETRICALLY SUBSTITUTED "ELECTRON-RICH" OLEFINS

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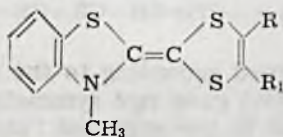
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Reakcję heterocyklicznych soli oniowych **4**, **6a** i **6b** z odpowiednimi 2-piperidynopochodnymi **5a**, **5b** i **7** zastosowano do otrzymywania niesymetrycznych alkenów zawierających dwa różne układy heterocykliczne. W dyskusji wykazano, że przebieg tej reakcji zależy od kwasowości użytej soli oniowej.

Реакция гетероциклических онёвых солей **4**, **6a** и **6b** с 2-пиперидинопроизводными **5a**, **5b** и **7** была применена для получения несимметричных алкенов, содержащих две различных гетероциклических системы. В дискуссии показано, что механизм этой реакции зависит от кислотности онёвой соли.

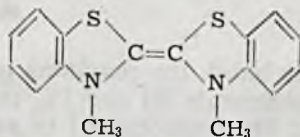
The reaction of heterocyclic onium salts **4**, **6a** and **6b** with corresponding 2-piperidine derivatives **5a**, **5b** and **7** was applied for preparation of unsymmetrical olefins containing two different heterocyclic systems. The course of above reaction depending on acidity of used salt was discussed.

In previous communication¹⁾ we have briefly reported the synthesis of "electron-rich" olefins (**1a** and **1b**) with double bond connected with two different heterocyclic systems: one of them being derived from thiazole system and the other — from 1,3-dithiole system. These alkenes were prepared in order to test their stability and reactivity in comparison with corresponding symmetrically substituted alkenes such as **2** and **3**.

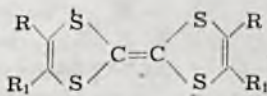


1a : R = R₁ = C₆H₅

1b : R/R₁ = —CH=CH—CH=CH—



2



3a : R = R₁ = C₆H₅

3b : R/R₁ = —CH=CH—CH=CH—

The unsymmetrical olefins **1a** and **1b** were obtained in the reaction of proper olium (onium) salt derived from one heterocyclic system with 2-piperidine derivative of the other system, adapting one of the methods of the symmetrical alkenes formation (**2**²⁾ and **3a**³⁾.

Two alternative procedures can be accepted for preparation of **1a** and **1b**: in the former thiazolium salt and piperidine derivative of 1,3-dithiole system are used as reagents, and in the latter 1,3-dithiolium salt and piperidine derivative of thiazole system are used as reagents.

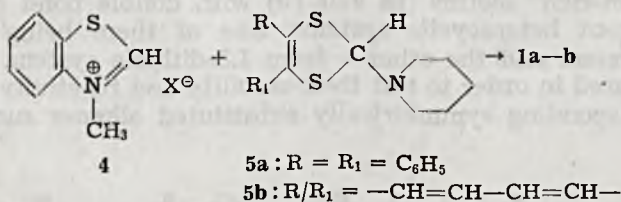
Table — Tablica

Results of reactions of onium (olium) salts with piperidine derivatives
Wyniki reakcji soli oniowych (oliowych) ze związkami piperydynowymi

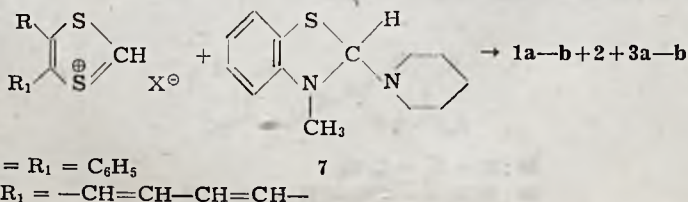
Experiment Doświadczenie	Salt Sól	Piperidine derivative Pochodna piperydynowa	Products (molar ratios) Produkty (stosunki molowe)		
			S=S	S=P	P=P
I	4	5a	—	1a (1.0)	—
II	4	5b	—	1b (1.0)	—
III	6a	7	3a (1.25)	1a (1.0)	2*
IV	6b	7	3b (1.65)	1b (1.0)	2*
V	6a	5b	3a (1.37)	9 (1.0)	3b (1.33)
VI	6b	5a	3b (2.40)	9 (1.0)	3a (2.05)

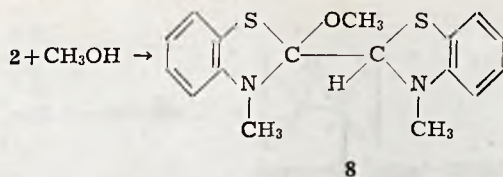
* Bis-(N-methylbenzothiazolynilidene-2) (**2**) was transformed into **δ** by treatment with methanol.

The "crossed" alkenes (**1a** or **1b**, respectively) were the only olefinic products of both reactions carried out according to the first procedure (Experiments I and II, the Table); no formation of symmetrical alkenes (**2** or **3**) was observed.



On the other hand, the reactions performed according to the second procedure (Experiments III and IV, the Table) gave two symmetrical olefins (**2** and **3a** or **3b**, respectively) in addition to the expected "crossed" compounds (**1a** or **1b**), the symmetrical products predominating.



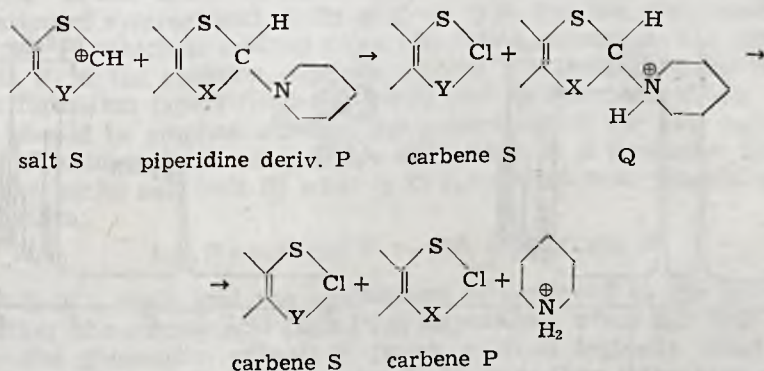


All the above reactions were carried on under the same conditions, using equimolar quantities of both reagents. The structure of olefins **1a** and **1b** was determined by elemental analysis and spectral data. Compounds **3a** and **3b** were identified by comparison with standard samples ^{4,5} and the unstable alkene **2**, which decomposed during chromatography, was identified as the product of methanol addition, i.e. compound **8** ².

The main problem of the present publication consists in the discussion on different courses and the mechanisms of the above reaction.

Pazdro and Polaczkowa ³ have demonstrated for some 2-amino-4,5-diphenyl-1,3-dithioles that they cleave in acidic medium with transient carbene formation. Using the same procedure we have measured NMR spectra of **5a**, **5b** and **7** in CH_3CN when acidified with a) CF_3COOH , and b) CF_3COOD . These spectra (Figure) show that the onium (olium) salts which are formed from piperidine compounds investigated are fully deuterated at C-2 when CF_3COOD is used, this indicating the intermediate carbene participation.

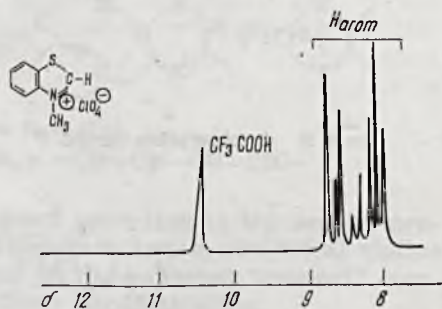
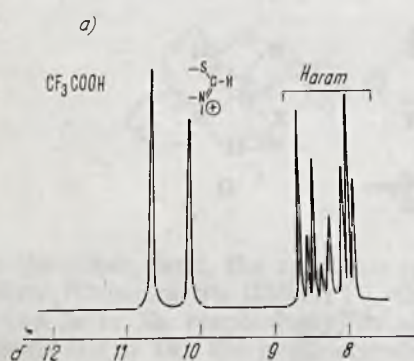
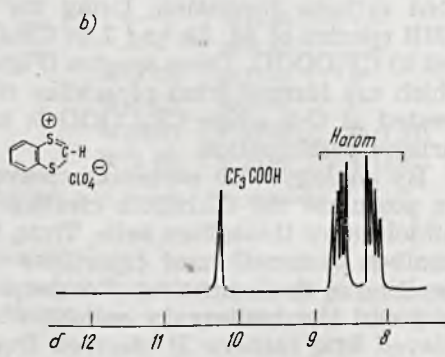
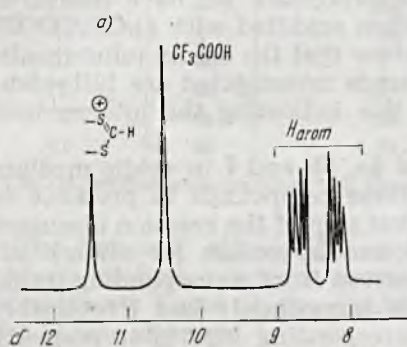
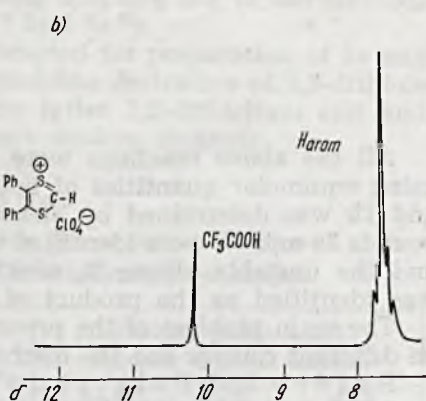
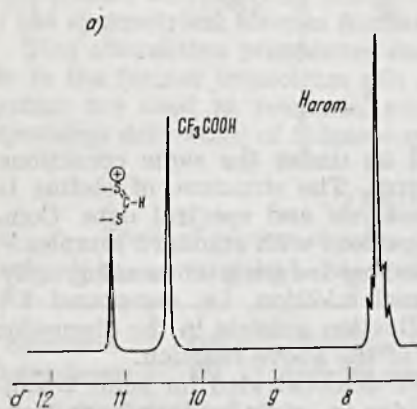
By analogy with carbenic cleavage of **5a**, **5b** and **7** in acidic medium we postulate the carbenic cleavage of these compounds in presence of dithiolium or thiazolium salts. Thus, the first step of the reaction discussed involves protonation of piperidine compound by onium (or olium) salt resulting in the formation of carbene S (derived from corresponding initial salt) and the quaternary salt Q which is immediately and irreversibly cleaved into carbene P (derived from corresponding piperidine reagent).



Experiments I and II: $\text{Y} = \text{N}-\text{CH}_3$, $\text{X} = -\text{S}-$

Experiments III and IV: $\text{Y} = -\text{S}-$, $\text{X} = \text{N}-\text{CH}_3$

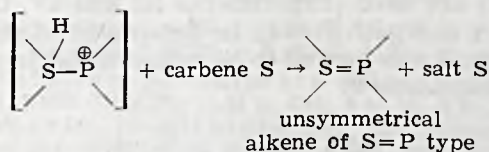
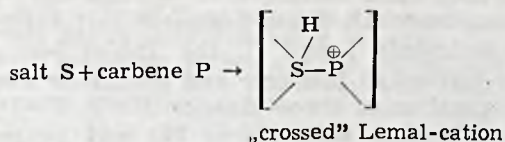
According to generally accepted pattern ^{6,7} the onium (olium) salt reacts with carbene yielding a transient Lemal-cation which is subsequently deprotonated into olefinic product. Two various pathways of reaction are possible in the case under discussion.



The NMR spectra of acetonitrile solutions of 2-piperidine-4,5-diphenyl-1,3-dithiole (5a), 2-piperidinebenzo-1,3-dithiole (5b) and 2-piperidine-N-methylbenzothiazoline (7):
 a — when acidified with CF₃COOH, b — when acidified with CF₃COOD

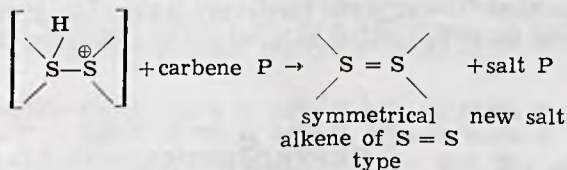
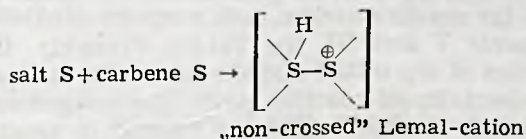
Widma NMR acetonitrylowych roztworów 2-piperidyno-4,5-dwufenyl-1,3-ditiolu (5a), 2-piperidynobenzo-1,3-ditiolu (5b) i 2-piperidyno-N-metylobenzotiazoliny (7):
 a — po zakwaszeniu CF₃COOH, b — po zakwaszeniu CF₃COOD

Path A:



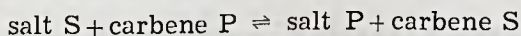
involving the reaction of carbene P with initial salt S to yield the "crossed" Lemal-cation which is deprotonated by carbene S resulting in formation of unsymmetrical olefin of S=P type and the regeneration of initial salt S.

Path B:



involving the reaction of carbene S with initial salt S to yield the "non-crossed" Lemal-cation which is deprotonated by carbene P resulting in formation of symmetrical olefin of S=S type and the generation of new salt (salt P) which is derived from piperidine substrate. The appearance of salt P in the reaction mixture affords the possibility for the P=P olefin formation (apart from the S=P) just as described above.

It should be emphasized that the generation of the new salt (salt P) in the reaction mixture is possible only when it is a weaker C—H acid than the initial salt (salt S) what is in agreement with general acid-base equilibrium:

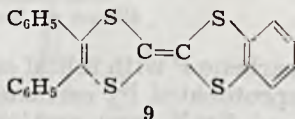


If salt S is a weak acid the equilibrium is displaced to the left and the formation of a strong acid (salt P) is impossible; when salt S is a strong acid — the generation of salt P (weak acid) is logically substantiated.

1,3-Dithiolium salts are stronger C—H acids than thiazolium salts are. This can be inferred from the position of C-2-H signals in their NMR spectra, and has been proved by measuring the rates of deuterium incorporation at C-2 of those salts. The half-lives of H/D exchange in 7.6 N CF₃COOD/D₂O at 25°C are: 58 min for **6a**, and 18 min for **6b**. The rate of H/D exchange for thiazolium salt **4** under the same conditions is too slow to be measured. The more detailed report on the H/D exchange rates in 1,3-dithiolium salts will be published in *Roczniki Chemii*⁸⁾.

Thus, the unsymmetrical olefins S=P are the only products of reactions in which thiazolium salt **4** and 2-piperidine-1,3-dithiole **5a** or **5b** are the reagents (Experiments I and II, the Table) because the new salt (salt P) cannot be formed in this case and path B is inadmissible. On the other hand, the formation of three alkenes (S=P, P=P and S=S) is observed when 1,3-dithiolium salts (**6a** or **6b**) and 2-piperidine-N-methylbenzothiazoline (**7**) are used (Experiments III and IV, the Table) because in this case path A and path B may be accomplished parallelly.

The above method was proved to be unsuccessful in preparation of unsymmetrical dithiolydene **9**:



It was found that three alkenes (one "crossed" and two symmetrical) are produced in the reactions when both reagents are derivatives of 1,3-dithiole (Experiments V and VI, the Table). Probably, the difference between the acidities of the initial and the new salts in this case is too small to enable the selectivity of reaction path. The comparison of molar ratios of symmetrical and "crossed" products formed in reaction V with those formed in reaction VI suggests, however, somewhat greater participation of path A when **6a** is the initial salt, which is a slightly weaker C—H acid than **6b**.

EXPERIMENTAL

General

NMR spectra were recorded on Jeol JNM-C-60 spectrometer using TMS ($\delta = 0$ ppm) as an internal standard, and mass spectra with LKB-8000 spectrometer (direct probe, 70 eV). For TLC Silica Gel G (Serva) was used, and for column chromatography MN-Kieselgel (100—200 mesh) ASTM was applied. All melting points were uncorrected. R_f values concern TLC chromatograms.

Preparation of substrates

N-Methylbenzothiazolium methylsulfate: 27.0 g (0.20 mole) of benzothiazole, 25.2 g (0.20 mole) of $(\text{CH}_3)_2\text{SO}_4$ in 150 ccm of benzene were refluxed for 0.5 hr. The precipitated crystals were filtered off and crystallized from acetone. There was obtained 41.5 g (80%) of colorless needles, m.p. 131—132°C (Lit.⁹): 103°C). NMR (CH_3CN): 10.16 (s, CH), 8.41—7.51 (m, 4 H_{arom}), 4.29 (s, CH_3).

Analysis:

For $\text{C}_9\text{H}_{11}\text{NO}_4\text{S}_2$ (261.2) — Calcd.: 41.7% C, 4.2% H, 5.4% N, 24.5% S;
found: 41.6% C, 4.3% H, 5.3% N, 24.2% S.

N-Methylbenzothiazolium perchlorate (**4**) was prepared according to¹⁰, m.p. 147—148°C (Lit.¹⁰): 145—146°C). NMR (CH_3CN): 10.10 (s, CH), 8.45—7.25 (m, 4 H_{arom}), 4.42 (s, CH_3).

Analysis:

For $\text{C}_9\text{H}_8\text{NO}_4\text{SCl}$ (249.6) — Calcd.: 38.5% C, 3.2% H, 5.6% N, 12.8% S;
found: 38.3% C, 3.2% H, 5.6% N, 12.8% S.

2-Piperidine-N-methylbenzothiazoline (7): The suspension of N-methylbenzothiazolium methylsulfate (2.61 g, 0.01 mole) in 50 ccm of benzene was refluxed and 2.55 g (0.03 mole) of piperidine was added with stirring. After 0.5 hr the solution was cooled and washed with water to obtain the neutral reaction of water layer, dried over anhydrous $MgSO_4$ and the solvent was evaporated in vacuum. The residue was crystallized from petroleum ether yielding 2.1 g (90%) of 7, m.p. 63—64°C (Lit.²): 88°C). NMR (CCl_4): 6.90—6.40 (m, 4 H_{arom}), 5.95 (s, CH), 2.90 (s, CH_3), 2.35 (m, $2 \times CH_2$), 1.50 (m, $3 \times CH_2$).

Analysis:

For $C_{13}H_{12}NS_2$ (234.2) — Calcd.: 66.7% C, 7.7% H, 11.9% N, 13.7% S;
found: 66.3% C, 7.9% H, 11.7% N, 13.3% S.

Benzo-1,3-dithiolium perchlorate (6b) was prepared according to ⁵, m.p. 185°C (explosion). NMR (CH_3CN): 11.56 (s, CH), 8.40 (m, 4 H_{arom}).

2-Piperidinebenzo-1,3-dithiole (5b): The suspension of 6b (2.52 g, 0.01 mole) in 50 ccm of dry benzene was refluxed under argon and 2.55 g (0.03 mole) of dry piperidine was added with stirring. After 0.5 hr the solution was cooled and washed with water to obtain the neutral reaction of water layer, dried over $MgSO_4$ and the solvent was evaporated in vacuum. The crude product was dissolved in heptane and chromatographed on column as follows: heptane—benzene 2:1 and 1:1 eluted 0.6 g (40%) of *o*-di(benzo-1,3-dithiolythio)benzene, m.p. 128—130°C, which identity was stated by comparison of TLC with that of standard sample ⁵): R_f = 0.90 (benzene); heptane—benzene 1:2 eluted 1.0 g (42%) of 5b, m.p. 87—89°C. R_f = 0.50 (benzene). NMR (CCl_4): 6.97—6.85 (m, 4 H_{arom}), 6.0 (s, CH), 2.45 (m, $2 \times CH_2$), 1.45 (m, $3 \times CH_2$).

Analysis:

For $C_{12}H_{15}NS_2$ (237.2) — Calcd.: 60.8% C, 6.3% H, 5.9% N, 27.0% S;
found: 60.4% C, 6.6% H, 5.6% N, 26.4% S.

2-Piperidine-4,5-diphenyl-1,3-dithiole (5a) was prepared according to ¹¹, m.p. 120—121°C (Lit.¹¹): 110—111°C), R_f = 0.50 (benzene). NMR (CCl_4): 7.13 (s, 10 H_{arom}), 5.90 (s, CH), 2.75 (m, $2 \times CH_2$), 1.49 (m, $3 \times CH_2$).

Analysis:

For $C_{20}H_{21}NS_2$ (339.3) — Calcd.: 70.8% C, 6.2% H, 4.1% N, 18.8% S;
found: 71.0% C, 6.4% H, 4.0% N, 18.5% S.

4,5-Diphenyl-1,3-dithiolium perchlorate (6a): The solution of 60% $HClO_4$ (2 ccm) in 20 ccm of acetone was cooled in ice-salt bath and 0.34 g (0.001 mole) of 5a in 5 ccm of acetone was added. The crystals of 6a were separated when 100 ccm of dry ether was added. They were filtered off and washed with ether— $HClO_4$ (300:1). The yield 0.34 g (96%), m.p. 189—190°C (Lit.⁴): 190°C). NMR (CH_3CN): 11.15 (s, CH), 7.52 (s, 10 H_{arom}).

Analysis:

For $C_{15}H_{11}O_4S_2Cl$ (354.7) — Calcd.: 50.8% C, 3.1% H, 18.1% S;
found: 50.8% C, 3.3% H, 17.8% S.

Preparation of standard samples

Bis-(4,5-diphenyl-1,3-dithiolylidene-2) (3a) was prepared according to ⁴, m.p. 262—264°C (Lit.⁴): 262—263°C). R_f = 0.40 (heptane—benzene 3:1). NMR (CS_2): 7.16 (s, H_{arom}).

Analysis:

For $C_{30}H_{20}S_4$ (508.5) — Calcd.: 70.9% C, 3.9% H, 25.2% S;
found: 70.7% C, 4.1% H, 24.8% S.

Bis-(benzo-1,3-dithiolylidene-2) (3b) was prepared according to ⁵, m.p. 236—238°C (Lit.⁵): 236—240°C). R_f = 0.60 (heptane—benzene 3:1). NMR (CS_2): 6.98 (m, H_{arom}).

Analysis:

For $C_{14}H_8S_4$ (304.4) — Calcd.: 55.2% C, 2.6% H, 42.1% S;
found: 54.9% C, 2.9% H, 41.9% S.

N-Methyl-2-methoxy-2-(N-methyl-2-benzothiazoliny)-benzothiazoline (8) was prepared according to²⁾, m.p. 135–136°C (Lit.²⁾: 171°C and⁷⁾ 137°C. $R_f = 0.45$ (benzene—methanol 13:1). NMR (CS₂): 7.15–6.1 (m, 8 H_{arom}), 5.30 (s, CH), 3.11 (s, OCH₃), 2.86 (s, NCH₃), 2.81 (s, NCH₃).

Analysis:

For C₁₇H₁₈N₂OS₂ (330.3) — Calcd.: 61.8% C, 5.5% H, 8.5% N, 19.4% S;
found: 61.7% C, 5.5% H, 8.5% N, 19.1% S.

Reactions of onium (olium) salts with piperidine compounds

Experiments I and II

A sample of 0.25 g (0.001 mole) of N-methylbenzothiazolium perchlorate (4) and 0.001 mole of 5a (Exp. I) or 5b (Exp. II) in 50 ccm of CH₃CN were heated at 70°C under argon for 1 hr*. The solvent was evaporated to dryness. The crude product was dissolved in benzene and passed through a short column with silica gel. Most of benzene was removed in vacuum and some of CH₃OH was added; separated crystals were pure products. There was obtained 0.30 g (75%) of 1a (Exp. I) and 0.18 g (61%) of 1b (Exp. II).

2,2'-(N'-Methylbenzothiazolynylidene)-4,5-diphenyl-1,3-dithiolyidene (1a): red crystals, m.p. 163–164°C, $R_f = 0.80$ (benzene—methanol 13:1). NMR (CS₂): 7.05–6.52 (m, 14 H_{arom}), 3.45 (s, NCH₃). MS: $m/e = 403$ (85%, M⁺), 388 (100%), 178 (29%), 149 (18%).

Analysis:

For C₂₃H₁₇NS₃ (403.4) — Calcd.: 68.5% C, 4.2% H, 3.5% N, 23.8% S;
found: 68.7% C, 4.6% H, 3.4% N, 23.4% S.

2,2'-(N'-Methylbenzothiazolynylidene)-1,3-benzothiazolyidene (1b): orange crystals, m.p. 179–180°C, $R_f = 0.65$ (benzene—methanol 13:1). NMR (CS₂): 6.90 (m, 8 H_{arom}), 3.50 (s, NCH₃). MS: $m/e = 301$ (74%, M⁺), 286 (100%), 254 (7%), 178 (8%), 152 (5%).

Analysis:

For C₁₅H₁₁NS₃ (301.3) — Calcd.: 59.8% C, 3.7% H, 4.6% N, 31.9% S;
found: 59.7% C, 3.9% H, 4.4% N, 31.7% S.

Experiments III and IV

A sample of 0.001 mole of 1,3-dithiolium perchlorate 6a (Exp. III) or 6b (Exp. IV) and 0.234 g (0.001 mole) of 2-piperidine-N-methylbenzothiazoline (7) in 50 ccm of CH₃CN were heated at 70°C under argon for 1 hr. After cooling 30 ccm of CH₃OH was added** and the solution was refluxed for additional 0.5 hr. The solvent was evaporated in vacuum. The residue was dissolved in benzene and chromatographed on column as follows: benzene eluted: 0.127 g (25%) of 3a (Exp. III) or 0.085 g (28%) of 3b (Exp. IV); benzene—methanol (13:1) eluted: 0.080 g (20%) of 1a (Exp. III) or 0.051 g (17%) of 1b (Exp. IV); benzene—methanol (2:1) eluted 8 (yield not determined). The identity of all products was stated by comparison of their m.p. and TLC chromatograms with those of standard samples.

Experiments V and VI

A sample of 0.001 mole of 1,3-dithiolium perchlorate (6a in Exp. V or 6b in Exp. VI) and 0.001 mole of 2-piperidine-1,3-dithiole (5b or 5a, respectively) in 50 ccm of CH₃CN were heated at 70°C under argon for 1 hr. After cooling the solvent was

* Lack of 2 in the reaction mixture was stated by negative methanol test; see footnote**.

** Bis-(N-methylbenzothiazolynylidene-2) (2) was transformed into 8 by methanol addition; 8 can be chromatographically stated (TLC) or isolated. In this way we have stated the formation or lack of 2 in the reaction products (so-called methanol test for 2).

evaporated in vacuum. In both experiments TLC chromatograms consisted of three spots not very well separated. Their R_f values were: 0.40, 0.50, and 0.60 (heptane—benzene 3:1) thus showing the formation of three products. Their separation was performed using preparative TLC. Heptane—benzene (3:1) was used as the solvent system for developing of chromatograms. The chromatography afforded: Exp. V: 0.085 g (28%) of **3b**, 0.147 g (29%) of **3a** and 0.085 g (21%) of **9**; Exp. VI: 0.100 g (33%) of **3b**, 0.137 g (27%) of **3a** and 0.053 g (13%) of **9**.

3a and **3b** were identified by comparison with standard samples. The structure of **9** was determined by mass spectrum only because the elemental analysis was not fully correct and suggested slight contamination with **3a** and/or **3b**. MS: $m/e = 406$ (100%, M^+), 242 (34%), 178 (48%), 152 (48%), 121 (45%), 108 (28%).

Cleavage of 2-piperidine derivative **5a**, **5b** and **7** in acidic medium

A sample of 0.3 mmole of **5a**, **5b** or **7** was dissolved in 1 ccm of CH_3CN in NMR tube. NMR spectra were recorded immediately when a) 0.02 ccm of CF_3COOH and b) CF_3COOD was added. These spectra are recorded in the Figure. Analogous results were obtained when C_2Cl_4 or $CHCl=CCl_2$ were applied as the solvents.

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**SYNTEZA NIESYMETRYCZNIE PODSTAWIONYCH
„BOGATYCH W ELEKTRONY” OLEFIN**

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Opracowano metodę otrzymywania alkenów zawierających w cząsteczce dwa różne układy heterocykliczne, których budowa sugeruje możliwość reagowania jako tzw. „bogaty w elektrony” olefin. Otrzymano dwa takie związki: 2,2'-(N'-metylobenzotiazolinylieno)-4,5-dwufenylo-1,3-ditioliliden (**1a**), i 2,2'-(N'-metylobenzotiazolinylieno)-benzo-1,3-ditioliliden (**1b**) w reakcjach nadchloranu N-metylobenzotiazoliowego (**4**) i odpowiednio: 2-piperydino-4,5-dwufenylo-1,3-ditiolu (**5a**) lub 2-piperydynobenzo-1,3-ditiolu (**5b**). Oba alkeny powstawały z dobrymi wydajnościami (75% i 61%), a ponadto w obu reakcjach nie zaobserwowano tworzenia się alkenów o budowie symetrycznej, tj. związków **2** lub **3**. Natomiast jeśli substratami reakcji były nadchloran 4,5-dwufenylo-1,3-ditioliowy (**6a**) lub nadchloran benzo-1,3-ditioliowy (**6b**) oraz 2-piperydino-N-metylobenzotiazolina (**7**), wtedy obok alkenów **1a** lub **1b** powstawały również oba alkeny o budowie symetrycznej, tj. **2** i **3a** lub **2** i **3b**.

W celu wyjaśnienia różnych sposobów reagowania związków piperydynowych z solami oniowymi i oliowymi podjęto następujące doświadczenia. Przede wszystkim ustalono sposób rozpadu badanych związków piperydynowych **5a**, **5b** i **7** w środowisku kwaśnym mierząc widma NMR ich roztworów w CH_3CN po zakwaszeniu a) CF_3COOH i b) CF_3COOD (rysunek). Okazało się, że sole oniowe (oliowe) powstające w tych warunkach zawierały deuter przy C-2, gdy roztwór zakwaszono CF_3COOD , co oznacza, że podczas rozpadu związków piperydynowych przejściowo powstaje karben. Ponadto oznaczono półokresy wymiany H/D w 7,6 n $\text{CF}_3\text{COOD} - \text{D}_2\text{O}$ w temp. 25°, uzyskując dla nadchloranu benzo-1,3-ditioliowego (**6b**) $\tau_{1/2} = 18$ min, a dla nadchloranu 4,5-dwufenylo-1,3-ditioliowego (**6a**) $\tau_{1/2} = 58$ min. Nadchloran N-metylobenzotiazoliowy (**4**) w tych warunkach nie ulegał wymianie H/D w sposób zauważalny.

Biorąc pod uwagę wyniki powyższych doświadczeń oraz uwzględniając powszechnie przyjęty schemat powstawania alkenów z soli oniowych (oliowych) w obecności zasad, zaproponowano wyjaśnienie obserwowanych różnic w przebiegu badanych reakcji. Wykazano, że jeśli wyjściową solą jest sól tiazoliowa (słaby C—H kwas), wówczas w środowisku reakcji nie może powstać kwas mocniejszy od niej, tj. sól ditioliowa. Wtedy reakcja biegnie jednokierunkowo, dając jeden produkt — alken o budowie niesymetrycznej (droga A). Jeśli natomiast wyjściowa sól jest mocniejszym C—H kwasem (sól ditioliowa), wówczas może wytwarzać się kwas słabszy od niej (sól tiazoliowa), co stwarza możliwość drugiego sposobu reagowania (droga B); w tym przypadku uzyskuje się mieszaninę trzech produktów reakcji.