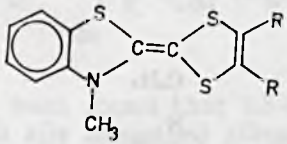
ROCZNIKI CHEMII
ANN. SOC. CHIM. POLONORUM
50, 2007 (1976)

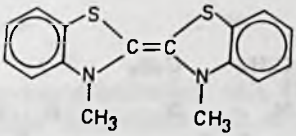
REACTIONS OF ELECTRON-RICH OLEFINS WITH OLIUM (ONIUM) SALTS

REAKCJE BOGATYCH W ELEKTRONY OLEFIN Z SOLAMI OLIOWYMI (ONIOWYMI)

In our previous paper [1] we have described the synthesis of unsymmetrically substituted "electron-rich" olefins, **1a** and **1b** that were prepared in order to test their stability and reactivity in comparison with symmetrical alkenes, such as **2**, **3a—c** and **4**.



1a : R = C_6H_5
1b : R/R = fused benzene ring



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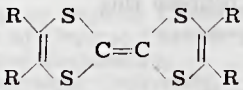
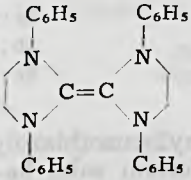


3a : R = C_6H_5
3b : R/R = fused benzene ring
3c : R = CH_3



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We have used the following olium and onium salts as electrophilic reagents to establish the reactivity of above alkenes: 4,5-diphenyl-1,3-dithiolium (**5a**), benzo-1,3-dithiolium (**5b**), 4,5-dimethyl-1,3-dithiolium (**5c**), N-methylbenzothiazolium (**6**), N-ethylbenzothiazolium (**6a**), 1,3-diphenylimidazolinium (**7**) and 1,3-dimethylbenzoimidazolium (**7a**) perchlorates. The results of these reactions are listed in the Table.

It has been found that the most reactive alkene, i.e. bis(1,3-diphenylimidazolidinylidene-2) (**4**) reacts easily during 5 hrs with 1,3-dithiolium salts **5a—c**, yielding 1,3-diphenylimidazolinium salt (**7**) and alkene **3a—c** (according to Schema (1)).

Table — Tablica

Products of reaction of „electron-rich" olefins with olium (onium) salts*

Produkty reakcji „bogatych w elektrony" olefin z solami oliowymi (oniowymi)*

Alkene	Salt						
	5a	5b	5c	6	6a	7	7a
4	3a+7	3b+7	3c+7	2**+7			4*
2***	3a+6	3b+6	3c+6		4*	4*	
1a	3a+6	5*	4*	4*		4*	
1b	5*	3b+6	4*	4*		4*	
3c	3a+5c	3b+5c	4*	4*		4*	

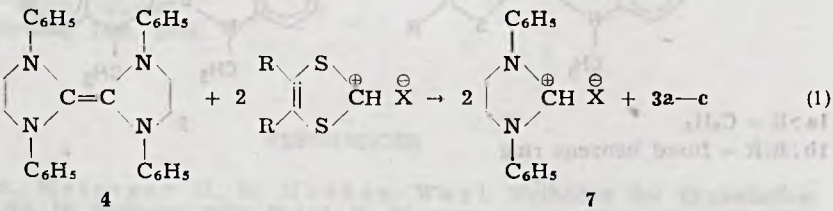
* All reactions were carried on in acetonitrile at 70°C under argon during 5—10 hrs. Pure products were isolated in high yields and identified by TLC, spectral data and elemental analyses — Reakcje prowadzono w acetonitrylu, w atmosferze argonu, w ciągu 5—10 godzin. Produkty wydzielono z dużymi wydajnościami i identyfikowano chromatograficznie, na podstawie danych spektralnych i analizy elementarnej.

** Compound 2 was converted into N-methyl-2-methoxy-(N-methyl-2-benzothiazolinyl)-benzothiazoline (8) by treatment with methanol — Związek 2 przeprowadzono w N-metylo-2-metoksy-(N-metylo-2-benzotiazolinylo)-benzotiazolinę (8) działając metanolem.

*** Compound 2 was generated in the reaction mixture from its methanol adduct 8 — Związek 2 generowano bezpośrednio w mieszaninie reakcyjnej z adduktu 8.

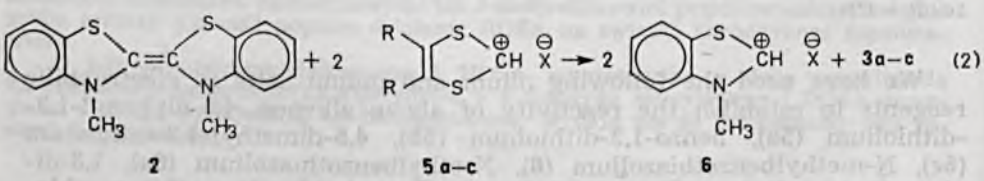
4* No reaction has been observed — Reakcja nie zachodzi.

5* Reaction has not been finished yet — Reakcja niedokończona.

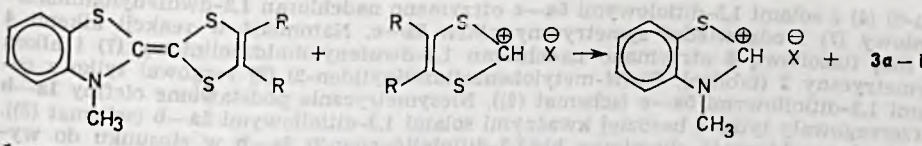


5a : R = C_6H_5
5b : R/R = fused benzene ring
5c : R = CH_3

Bis(N-methylbenzothiazolynylidene-2) (2) reacts with similar facility with 1,3-dithiolium salts 5a—c yielding thiazolium salt (6) and alkene 3a—c (according to Schema (2)).



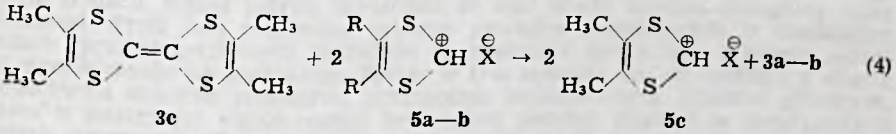
The "crossed" olefins, 1a and 1b, appeared to be somewhat less reactive than 2: they react with 5a and 5b in the same way as described above, while with 4,5-dimethyl-1,3-dithiolium salt (5c) no reactions has been observed (Schema (3)).



1a : R = C_6H_5 **5a—b** **6**
1b : R/R = fused benzene ring

Our previous experiments [2] have shown that bis(1,3-dithiolylidenes-2), **3a** and **3b**, are completely passive towards many electrophils. We have found that these alkenes are not attacked by any 1,3-dithiolium salts **5a—c** investigated.

On the other hand, bis(4,5-dimethyl-1,3-dithiolylidene-2) (**3c**), when heated for 10 hrs with **5a** or **5b**, yielded 4,5-dimethyl-1,3-dithiolium salt (**5c**) and **3a** or **3b**, respectively. It should be emphasized that it is the first example of reaction in which bis(1,3-dithiolylidene-2) behaves like a dimer of nucleophilic carbenes (Schema (4)).



3c **5a—b** **5c**

It has been found that 1,3-diphenylimidazolinium salt (**7**) does not react with any examined alkenes, while thiazolium salt **6** reacts with bis(1,3-diphenylimidazolidinylidene-2) (**4**) only.

The results of these experiments suggest that the reactivity of "electron-rich" olefins depends mainly on heteroatoms adjacent to double bond, but also on the electrophilic properties of reagents used.

A more detailed report on this problem will be published in *Roczniki Chemii.*

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REFERENCES

1. Buza D., Krasuski W., *Roczniki Chem.*, **49**, 2007 (1975).
2. Buza D., Pazdro K., Szymański S., unpublished papers.

STRESZCZENIE

Zbadano reakcje „bogatych w elektrony" olefin **1a—b**, **2**, **3a—c** i **4** z solami 1,3-ditioliowymi **5a—c**, tiazoliowymi **6**, **6a** i 1,3-dwufenyloimidazoliniową **7**. Reakcje prowadzono w atmosferze argonu, w acetonitrylu, w temperaturze 70°, w ciągu 5—10 godzin. W reakcji najbardziej reaktywnego bis(1,3-dwufenyloimidazolidynylide-

nu-2) (**4**) z solami 1,3-ditiolowymi **5a—c** otrzymano nadchloran 1,3-dwufenyloimidazoliniowy (**7**) i odpowiedni symetryczny alken **3a—c**. Natomiast w reakcji alkenu **4** z solą tiazoliową **6** otrzymano nadchloran 1,3-dwufenyloimidazoliniowy (**7**) i alken symetryczny **2** (tablica). Bis(N-metylobenzotiazolinyliden-2) (**2**) reagował tylko z solami 1,3-ditioliowymi **5a—c** (schemat (2)). Niesymetrycznie podstawione olefiny **1a—b** przereagowały tylko z bardziej kwaśnymi solami 1,3-ditioliowymi **5a—b** (schemat (3)). Stwierdzono bierność chemiczną bis(1,3-ditiolylidenów-2) **3a—b** w stosunku do wymienionych soli, w przeciwieństwie do bis(4,5-dwufenylo-1,3-ditiolylidenu-2) (**3c**), który reagował z solami 1,3-ditioliowymi **5a—b** (schemat (4)). Żaden z badanych dimerów nie reagował z nadchloranem 1,3-dwufenyloimidazoliniowym (**7**). Wysunięto postulat, że reaktywność bogatych w elektrony olefin zależy zarówno od kwasowości użytej soli oliowej (oniowej), jak i od budowy alkenu.

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