Tetrahedron Letters No. 38, pp 3413 - 3414, 1976. Pergamon Press. Printed in Great Britain.

SULFONIUM YLIDE DIMERIZATION: A NOVEL ROUTE TO UNSATURATED TETRADENTATE SULFUR LIGANDS

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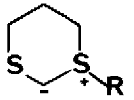
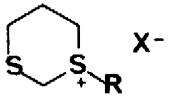
(Received in USA 26 July 1976; received in UK for publication 9 August 1976)

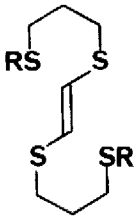
In connection with another study, we had occasion to prepare the ylide 1a from 1-cyclopropylcarbinyl-1,3-dithianium tetrafluroborate[1] 2a. Although sulfonium salts 2b-c have been reported previously,[2] there have been no reports in the literature concerning the corresponding ylides of dithiane other than allylic ylides which undergo [2,3] sigmatropic rearrangement.[3] We have found that the ylides 1a-c undergo a facile dimerization yielding bis-thioethylenes 3a-c [NMR: 6.22 δ(2H-s)] and 4a-c [NMR: 6.12 δ(2H-s)] in good yields.



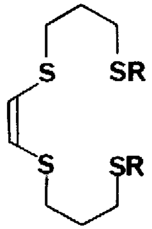
1a R= CH$_2$-◁
1b R= CH$_3$
1c R= Et



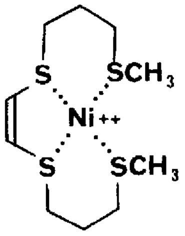
2a R= CH$_2$-◁ , X= BF$_4$
2b R= CH$_3$, X= I
2c R= Et , X= I



3a R= CH$_2$-◁
3b R= CH$_3$
3c R= Et



4a R= CH$_2$-◁
4b R= CH$_3$
4c R= Et



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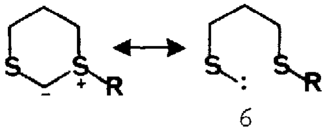
(Table I.) The cis and trans isomers are easily separable by chromatography on silica gel (4% ether/petroleum ether; Rf_{cis}= 0.08, Rf_{trans}=0.13). Cis-isomer 4b readily forms the red nickel complex 5 ($Ni(ClO_4)_2/CH_3NO_2$). Although many saturated tetradentate sulfur ligands have been reported[4] only a few unsaturated ligands such as 5 have been prepared[5] by alkylation of nickel bisdithienes. The unsaturated sulfur complexes are of interest because of their potentially useful electron transfer properties.[6] Although dimers **3** and **4** were usually prepared by treatment of the corresponding sulfonium salt with n-butyl lithium in THF at -78°, followed by warming to room temperature, the reaction also proceeds using NaH/DMF at room temperature making preparation of sizable quantities of **3** and **4** economical.

Table I

Salt	R	X	Ratio **3**/**4** (NMR)	% yield
2a	CH_2-◁	BF_4	40/60	59
2b	CH_3	I	28/72	78
2c	Et	I	34/66	79



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The mechanism of the dimerization reaction is now considered. α-Cleavage of sulfonium ylides yielding carbene-like dimers has been noted before[7] in acyclic cases. Notably, Johnson[8] and coworkers have reported that diphenyl sulfonium benzylide decomposes to give 78% <u>cis</u> and <u>trans</u>-stilbene. Thus, an attractive mechanism for the facile dimerization involves the intermediacy of a novel thiocarbene **6**.[9] However, when the dimerization is carried out in the presence of cyclohexene no cyclopropane could be detected.

<u>Acknowledgment</u>: We would like to thank the Department of Chemistry and the Indiana University Research Fund for financial support.

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6. G.N. Schrauzer, <u>Advances in Chemistry Series</u>, **110**, 73 (1972).
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