Tetrahedron Letters No.29, pp. 3327-3330, 1968. Pergamon Press. Printed in Great Britain.

Allylsulfonium Salts-Vinyl Ylides: Their Chemical Properties

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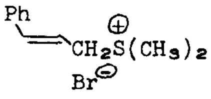
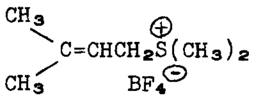
(Received in USA 15 March 1968; received in UK for publication 25 April 1968)

In continuation of our studies of sulfur ylides, we began to explore the preparation and reactions of vinyl sulfur ylides.[2] Our attention was focussed on these species because of their possible roles in carbon-carbon bond formation in biological systems leading to such products as squalene, chrysanthemic acid, the "nonisoprenoid" C_{10} oil of S. chamaecyparissus,[3] stearolic acid, etc. A recent report on the preparation of the ylide generated from γ,γ-dimethallyldimethylsulfonium bromide[4] prompts a preliminary report of our work in this area which also describes additional evidence supporting tetravalent sulfur intermediates.[2b]

We have prepared the sulfonium salts I, II, and III starting from the corresponding bromides.[5] Treatment of I or II with n-butyllithium at -78° and consequently warming to room temperature produces the corresponding rearrangement product IV. The structures of IV a and b were established by analysis[5] and spectral data - IV a: ir, 1635, 1600, and 1500 cm^{-1}; nmr, 1.95 p.p.m. (3H, S), 2.79 p.p.m. (2H, d, J=7Hz), 3.49 p.p.m. (1H, q, J=7Hz), 5.09 p.p.m. (1H, d further split, J=10 Hz), 5.02 p.p.m. (1H, d further split,



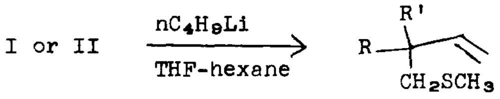
I



II

$CH_2{=}CHCH_2\overset{\oplus}{S}(Ph)_2\ \underset{}{BF_4^{\ominus}}$

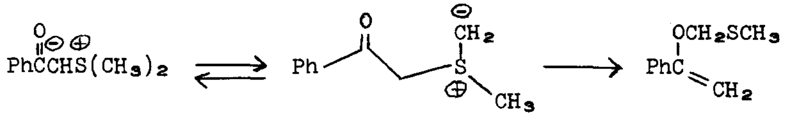
III



IV a) R = H, R' = Ph
b) R = R' = CH_3

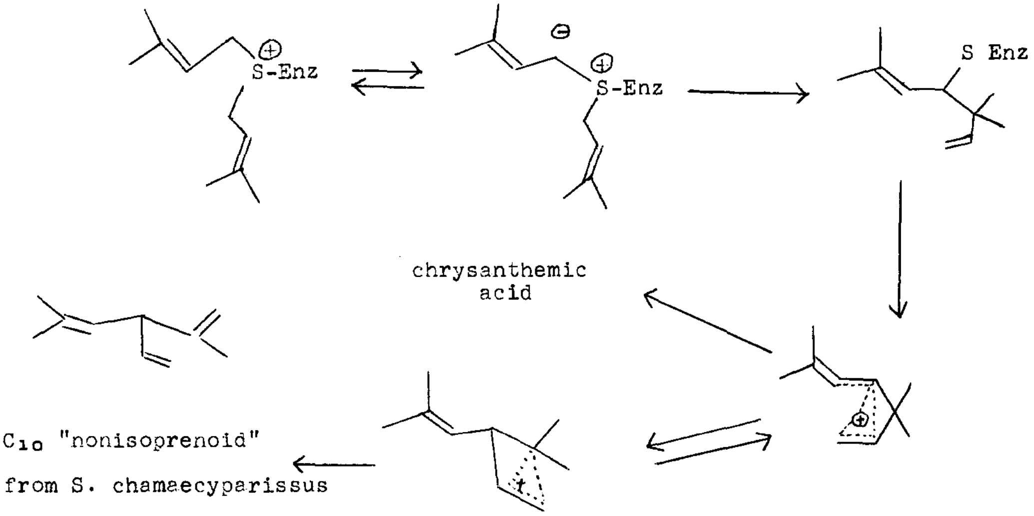
J=17 Hz), 6.05 p.p.m. (1H, m) and 7.20 p.p.m. (5H, s); ms, 178, 130, 117, 115, 91, 85, 83, 77, 61 - IV b: ir, 1640 cm^{-1}; nmr, 1.08 p.p.m. (6H, s), 2.07 p.p.m. (3H, s), 2.43 p.p.m. (2H, s), 4.90 p.p.m.)1H, d. of d., J=1.5 and 10 Hz), 4.94 p.p.m. (1H, d. of d., J=1.5 and 18 Hz), 5.85 (1H, d. of d., J=10 and 18 Hz).

This rearrangement is quite analogous to the rearrangement of dimethylsulfoniumphenacylide in aqueous media which we[6] and others observed.[7,8] It



is interesting to note that no 1,2 shift is observed. The fact that the rearrangement occurs so facilely lends credence to the role of these types of ylides in the head to tail isoprene dimers as found in chrysanthemic acid and the C_{10} oil of S. chamaecyparissus (scheme I).

Scheme I: Possible Biogenetic Pathway



To obviate the rearrangement, we generated the ylide from III which behaves as a normal vinyl ylide. Quenching with deuteroacetic acid produces >90% monodeuterated sulfonium salt in which no detectable amount of the diphenylpropenylsulfonium isomer was present. Thermal decomposition led to no α elimination. Attempts to observe cyclopropene formation under Closs's conditions also failed.[9] A detailed study of the reaction of n-butyllithium with this salt led to the products summarized in Table I. These results are best interpreted on the basis of tetravalent sulfur intermediates which extrudes the coupling product and forms an organosulfide. Such behavior has been well recognized in pentavalent phosphorus chemistry[10] and these experiments indicate that such reactivity may be a common mode of decomposition of tetravalent sulfur species.[11]

Table I: Volatile Products in the Generation of Diphenylsulfoniumallylide[a]

Compound	Relative %	Compound	Relative %
propene	11.4	_n_-butylbenzene	0.0
benzene	48.8	di-_n_-butylsulfide	1.4
1-heptene	0.0	allylphenylsulfide	1.7
octane	9.3	butylphenylsulfide	22.1
allylbenzene	0.0	biphenyl	5.3

a) Diphenylsulfide produced in 62% yield.

Acknowledgment: We are grateful for the support of the National Institutes of Health, GM - 13598, which enabled us to pursue these studies.

References

1. a) Alfred P. Sloan Foundation Fellow. b) National Institutes of Health Predoctoral Fellow.
2. a) This paper constitutes Part V in our series on Ylide Chemistry.
   b) For Part IV, see B. M. Trost and R. C. Atkins, *Tetrahedron Letters*, *No.* **10**, 1221 (1968); c) Part III, B. M. Trost, *J. Am. Chem. Soc*., **89**, 138 (1967); d) Part II, B. M. Trost, *Tetrahedron Letters*, *No.* **46**, 5761 (1966); e) Part I, B. M. Trost, *J. Am. Chem. Soc*., **88**, 1587 (1966).
3. A. F. Thomas and B. Willham, *Tetrahedron Letters*, *No.* **49**, 3775 (1964).
4. R. B. Bates and D. Feld, *Tetrahedron Letters*, *No.* **4**, 417 (1968).
5. All new compounds had satisfactory elemental analyses.
6. B. M. Trost, unpublished work.
7. K. W. Ratts and A. N. Yao, *J. Org. Chem*., **33**, 70 (1968).
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9. G. L. Closs and K. D. Krantz, *J. Org. Chem*., **31**, 638 (1966).
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11. Cf. E. J. Corey and W. Oppolzer, *J. Am. Chem. Soc*., **86**, 1899 (1964).