Tetrahedron Letters No.4, pp. 417-419, 1968. Pergamon Press. Printed in Great Britain.

VINYLSULFONIUM YLIDES AS POSSIBLE ENZYMIC INTERMEDIATES; EXCHANGE AND REARRANGEMENT OF A VINYLSULFONIUM YLIDE

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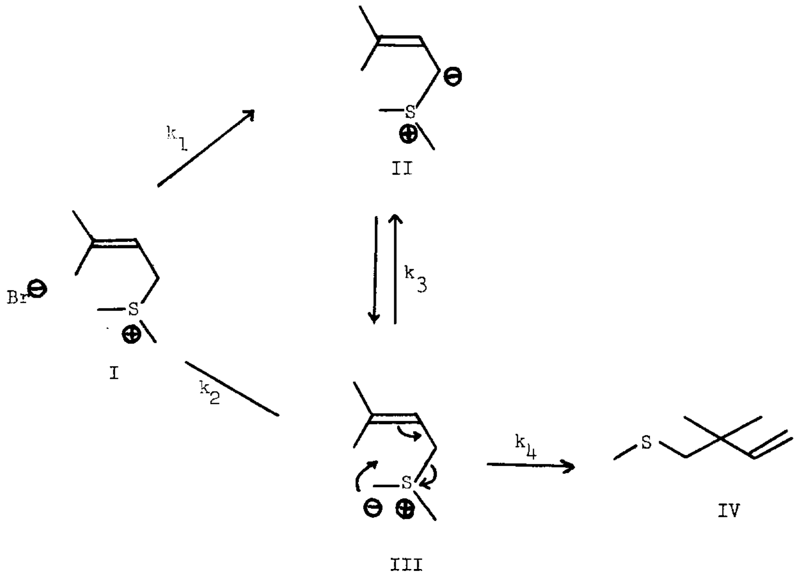
(Received in USA 2 October 1967)

Vinylsulfonium ylides of the type II are possible intermediates in several enzyme-catalyzed carbon-carbon bond forming reactions, such as the coupling reactions which produce squalene and phytoene, and the sequences by which the cyclopropane ring of chrysanthemic acid and the cyclopropene ring of sterculic acid are formed. Although the chemistry of vinylsulfonium ylides has not been investigated, the behavior of many closely related sulfonium ylides[2] makes these possibilities attractive. We have begun a study of vinylsulfonium ylides, and wish to report the first preparation of a vinylsulfonium ylide(II). II undergoes rapid proton transfer to an isomeric ylide III which rearranges in high yield to an isomeric homoallyl sulfide IV.



When γ,γ-dimethylallyldimethylsulfonium bromide(I) was treated with n-butyllithium in hexane-tetrahydrofuran at -78° and the reaction mixture warmed to 0° for workup, the homoallyl sulfide IV, isomeric with the desired ylide II, was isolated in 84% yield. The structure of IV is evident from its elemental analysis and spectral properties (n.m.r.: singlet, 8.9 τ, 6H; singlet, 7.9 τ, 3H; singlet, 7.5 τ, 2H; vinyl pattern, 4-5 τ, 2H. IR: 1645, 995, and 910 cm.$^{-1}$).

IV was apparently formed via rearrangement (arrows) of the undesired ylide III, formed directly by proton extraction from I or by exchange from the vinylsulfonium ylide II. To learn which ylide is formed first and to gain information regarding ylide exchange reactions, α,α-dideutero- γ,γ-dimethylallyldimethylsulfonium bromide was prepared via $LiAlD_4$ reduction of ethyl β,β-dimethylacrylate, conversion to the bromide with PBr_3, and reaction with dimethylsulfide. With n-butyllithium, this deuterated sulfonium salt gave butane containing 35% of the monodeuterated species; this indicates that the undeuterated sulfonium salt, in which there is no isotope effect (estimated at 6:1), gives the desired ylide II about 75% of the time (i.e., $k_1 > k_2$). The desired ylide II is statistically unfavored by a factor of 3, and without this factor it must be favored, undoubtedly by a resonance effect, by a factor of 9. The rearranged sulfide from this reaction was (by mass and n.m.r. spectra) a mixture of monodeuterated and dideuterated IV with the deuteriums in the terminal vinyl positions, showing that the ylide III rearranges faster than it is converted back to the ylide II (i.e., $k_4 > k_3$).

The rearrangement III → IV is analogous to the rearrangement of dimethylsulfonium phenacylide (C=O instead of C=C),[3] the sulfonium analog of the Sommelet-Hauser reaction (aryl instead of C=C),[4] and supports the mechanism of Parham and Groen for the reaction of allyl sulfides with dichlorocarbene to give substituted butadienes[5] and homoallyl sulfides containing chlorine.[6] The latter workers postulate that an intermediate ylide like III is formed and rearranges as shown.

In view of the ease with which allyl sulfonium salts like I can be prepared and the high yield observed in the rearrangement of I, this procedure should provide a useful synthetic route to many homoallyl sulfides.

We are exploring several obvious ways to avoid the II → III exchange so that other reactions of vinylsulfonium ylides like II can be studied.

Acknowledgements: Financial support from the Public Health Service (GM-11721) and the National Science Foundation is gratefully acknowledged.

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