

CYCLOADDITIONS. XXV. CYCLOADDUCTS FROM DIPHENYL SULFIDE AND ALLYLIC CHLORIDES<sup>1</sup>

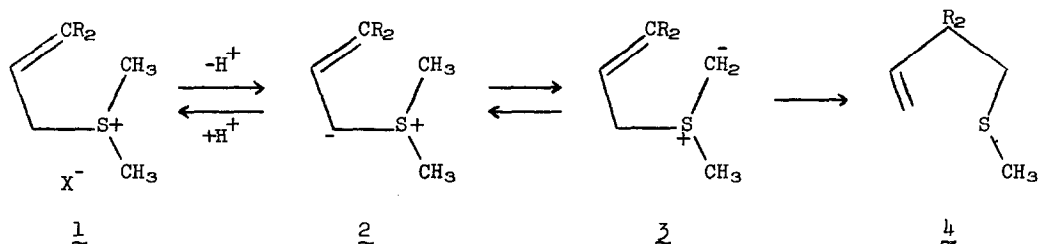
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The allyldimethylsulfonium salts 1 react with alkyllithium reagents to give allylcarbinyl methyl sulfides 4,<sup>4-8</sup> presumably through a Claisen-like rearrangement of the anion 3 involving 6 electrons disposed over 5 atomic centers.<sup>7,8</sup>

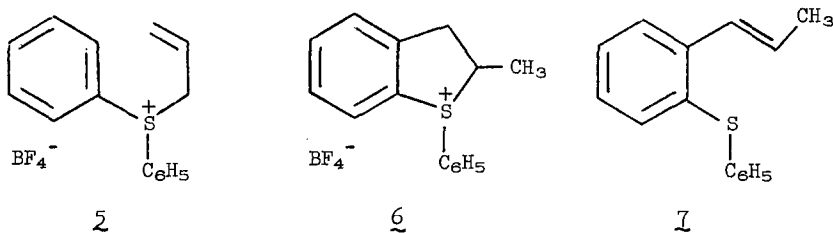


This reaction hampers chemical investigations of alkylidenesulfuranes 2; the equilibrium between the sulfuranes 2 and 3 is displaced irreversibly through the rearrangement 3  $\rightarrow$  4 before intermolecular reactions of 2 can be effected.

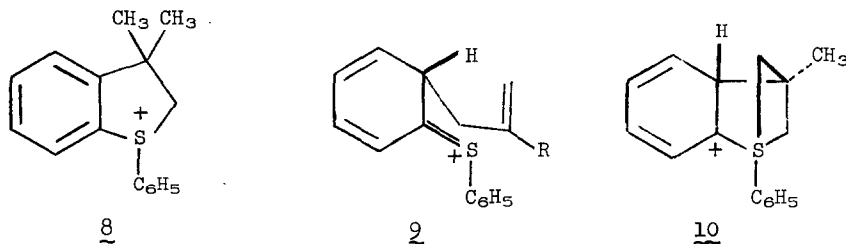
To obviate such rearrangements, allyldiphenylsulfonium tetrafluoroborate (5) was prepared and found to behave as a normal vinyl ylide, exhibiting behavior best interpreted on the basis of tetravalent sulfur intermediates.<sup>6</sup>

Our experience with attempts to prepare allyldiphenylsulfonium tetrafluoroborate has been quite different. Diphenyl sulfide and allyl chloride in 1,2-dichloroethane gave on treatment with silver tetrafluoroborate a 25% yield of crude salt, mp 135-145°. Recrystallization from  $\beta$ -pentanone gave an analytically pure sample of C<sub>15</sub>H<sub>15</sub>BF<sub>4</sub>S, mp 149.5-150°; nmr (CDCl<sub>3</sub>)  $\tau$  2.50

(m, 9), 6.55 (m, 1), 8.23 (d,  $J = 7$  Hz, 2) and 8.65 (d,  $J = 7$  Hz, 3). No bands attributable to a C-C double bond were observed in the infrared spectrum. (By contrast, allyldimethylsulfonium bromide has infrared absorptions at 1640 and 955  $\text{cm}^{-1}$  in  $\text{CHCl}_3$ .) This salt was formulated as the cycloadduct 6. Upon alkaline hydrolysis<sup>10</sup> it gave an oil identified as the aromatic sulfide 7; nmr  $\tau$  2.81 (m, 9), 3.11 (m, 1), 3.83 (m, 1), and 8.16 (doublet of doublets,  $J = 1.5$  and 6.5 Hz, 3); infrared band at 975  $\text{cm}^{-1}$  in  $\text{CCl}_4$ .



Methylallyl chloride and diphenyl sulfide gave under similar conditions a sulfonium salt having nmr absorptions at  $\tau$  2.60 (m, 9) and three singlets at 6.55, 8.17, and 8.58 (2:3:3). Formula 8 is the tentative structural assignment.



The reactions leading to salts 6 and 8 may be postulated as proceeding from the allyl-diphenylsulfonium salts through the Claisen rearrangement<sup>11-13</sup> product 9 to 6 and the intramolecular 1,3-cycloadduct 10 to 8. Other mechanistic possibilities, of course, obtain.

Confirmation of structural assignments for 6 and 8 is now being sought through synthesis of authentic samples.

References

1. Partial support of this work by the National Institutes of Health (GM 14381) is gratefully acknowledged.
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