Intramolecular Reactions of α- and β-Allylthioalkylcarbenes

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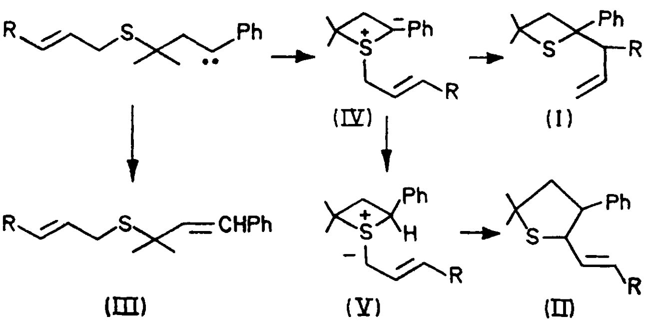
Summary The difference in products obtained from intramolecular reactions of α- and β-allylthioalkylcarbenes are attributable to formation of 3- and 4-membered cyclic ylides, respectively.

There has been considerable interest recently in intermolecular ylide formation from carbenes and sulphides.[1] However, no reliable evidence could be found in the literature on the related intramolecular ylides.[2] We now report definite evidence for the formation of thietanonium ylide from a carbene bearing a sulphide linkage on the β-carbon, and a ready thio-Claisen rearrangement of a simple allylvinyl sulphide derived from an α-allylthioalkylcarbene.

The β-allylthioalkylcarbene was generated by the photolysis of sodium salts of 3-crotylthio-3-methylbutyrophenone tosylhydrazone in monoglyme at 10°. Three products could be isolated from the photolysate in a total yield of 68·5%. Each of the components was roughly separated by column chromatography on silica and finally purified by preparative g.l.p.c. The identified products are 4,4-dimethyl-2-(1-methylallyl)-2-phenylthietan (I; 25·3%), 5,5-dimethyl-3-phenyl-2-prop-1-enyltetrahydrothiophen (II; 33·2%), and 3-crotylthio-3-methyl-1-phenylbut-1-ene (III; 41·5%). Thietan (I) was obtained as a mixture of diastereomers (56:44) and tetrahydrothiophen (II) was a mixture of *cis*- and *trans*-isomers (60:40).†

The formation of the thietan (I) clearly demonstrates the formation of a bond between carbene carbon and sulphur, *i.e.*, the intervention of thietanonium ylide (IV). The subsequent [2,3]sigmatropic rearrangement of the allylic sulphonium ylide (IV)[3] may afford the stable thietan (I). The relatively high-yield production of the tetrahydrothiophen (II) can also be rationalized by assuming the intervention of the ylide (IV). Thus, an ylide exchange reaction of (IV) to the exocyclic ylide (V) followed by Stevens-type rearrangement, may constitute the whole process.[4]



In sharp contrast with the case of β-crotylthioalkylcarbene, a completely different reaction was observed when an α-allylthioalkylcarbene was generated from sodium salts of α-allylthioacetophenone tosylhydrazone. In the latter case, the photolysis was carried out in monoglyme at −70°. A mixture of α- and β-allylthiostyrene [(VI) and (VII) in the ratio of 89:11], was obtained in almost quantitative yield. The observed n.m.r. spectrum clearly demon-

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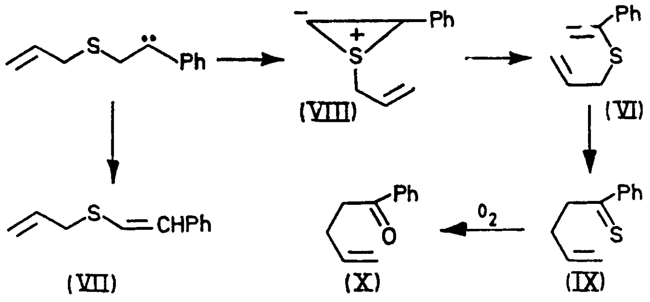
† The n.m.r. and mass spectra and elemental analyses of all new compounds were consistent with the structures assigned.

strates that the predominant component of the photolysate is olefin (VI). In this case, the episulphonium ylide (VIII) can also be assumed as an intermediate of the reaction.

When the photolysate was kept in the dark at room temperature for a few hours, an intense violet colour developed in the solution and its n.m.r. spectrum became completely different from that of (VI). The thermal product proved to be thioketone (IX), which was spontaneously transformed into ketone (X) under atmospheric conditions.



Although thio-Claisen rearrangements were observed in many systems,[5] none has previously been reported in the case of a simple allylvinyl sulphide. A recent report by Corey and Shulman[6] indicated that their attempted thermal thio-Claisen rearrangement of an $R_2C{=}CHSCH_2$-$CH{=}CH_2$ system at 160—180° was unsuccessful, and that mercuric oxide was found to be an effective catalyst to promote the rearrangement and produce aldehyde directly. In our system, however, the thio-Claisen rearrangement occurs quite smoothly at room temperature without the aid of any catalyst.

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[1] For example, W. Kirmse and M. Kapps, *Chem. Ber.*, 1968, **101**, 994, 1004; W. Ando, T. Yagihara, S. Tozune, and T. Migita, *J. Amer. Chem. Soc.*, 1969, **91**, 2786.

[2] Intramolecular reaction of hetero-atoms in carbenes has been reported, *cf.* W. Kirmse and M. Buschhoff, *Chem. Ber.*, 1967, **100**, 1491; J. H. Robson and H. Shechter, *J. Amer. Chem. Soc.*, 1967, **89**, 7112.

[3] J. E. Baldwin and R. E. Hackler, *J. Amer. Chem. Soc.*, 1969, **91**, 3646 and refs. therein.

[4] W. E. Parham and R. Koncos, *J. Amer. Chem. Soc.*, 1961, **83**, 4034.

[5] For example, D. J. W. Schuijl and L. Brandsma, *Rec. Trav. chim.*, 1968, **87**, 959; H. Kwart and T. J. George, *Chem. Comm.*, 1970, 433.

[6] E. J. Corey and J. I. Shulman, *J. Amer. Chem. Soc.*, 1970, **92**, 5522.