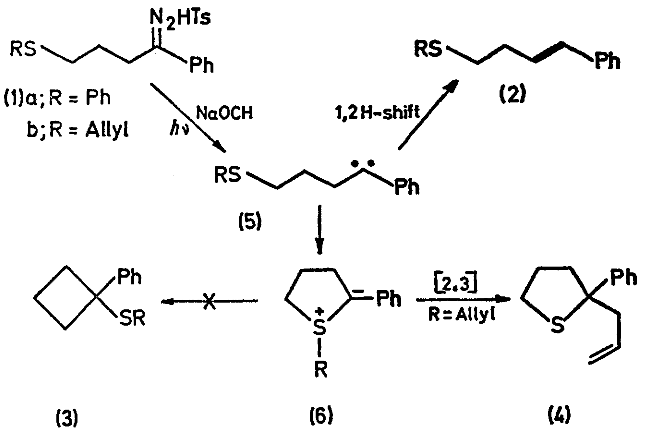
Reactions of Carbenes bearing Sulphide Linkages at the δ-Position

By Kiyosi Kondo* and Iwao Ojima
(*Sagami Chemical Research Centre,* 3100 *Onuma, Sagamihara,* 229 *Japan*)

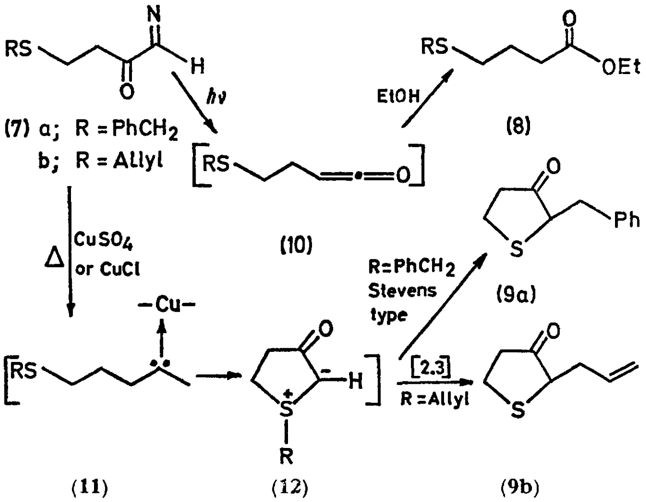
Summary The carbenes generated from γ-allylthiobutyrophenone tosylhydrazone and carbenoids from 4-benzyl- and 4-allyl-thio-1-diazobutan-2-one give thiolan and thiolanone derivatives, respectively, *via* cyclic sulphonium ylide intermediates.

There is currently much interest in labile ylides.[1] We have described[2,3] how carbenes bearing sulphide linkages at the β- or γ-positions produce small-ring ylides intramolecularly, *i.e.*, episulphonium and thietanonium ylides, and now report the reaction of homologous carbenes bearing sulphide linkages at the δ-position.†



γ-Phenylthiobutyrophenone tosylhydrazone (**1a**) was converted into the corresponding sodium salt in monoglyme and irradiated with light of wavelength >280 nm at 10° for 3 h. The only identifiable product was 4-phenylthio-1-phenylbut-1-ene (**2**) (*cis/trans* = 20/80) arising from 1,2-hydride shift (74·2% yield). Thus, the expected ring contraction[2] of the intermediate thiolanonium ylide (**6**) to cyclobutane (**3**) was not observed. On the other hand, irradiation of the sodium salt of γ-allylthiobutyrophenone tosylhydrazone (**1b**) in monoglyme at 10° afforded two products: 4-allylthio-1-phenylbut-1-ene (**2b**, 48·4% yield, *cis/trans* = 31·5/68·5) and 2-allyl-2-phenylthiolan (**4**, 26·2% yield). The formation of thiolan (**4**) can be explained by assuming the intermediate formation of thiolanonium ylide (**6**) followed by [2,3]sigmatropic rearrangement of the allylic moiety.‡

In order to exclude the 1,2-hydride shift, a carbonyl group was introduced into the α-position of the carbene. In this case, ylide formation and Wolff rearrangement would be competitive reactions. Irradiation of 4-benzylthio-1-diazobutan-2-one (**7a**) in ethanol at 10° for 2 h gave ethyl 4-benzylthiobutyrate (**8a**) in quantitative yield. Thus, the Wolff rearrangement of the intermediate keto-carbene is the only one of these processes occurring under photolytic conditions.[4] However, when the diazo-ketone (**7a**) was decomposed thermally in dioxan in the presence of a catalytic amount of anhydrous copper(II) sulphate, 2-benzylthiolan-3-one (**9a**) was obtained in 51% yield. A similar result was obtained when copper(I) chloride was used as catalyst. The formation of thiolan (**9a**) suggests that thermally generated carbenoid (**11a**) may also undergo an intramolecular addition to sulphur analogous to that undergone by (**5**), affording cyclic ylide (**12a**), which may rearrange to the final product.



Scheme

When 4-allylthio-1-diazobutan-2-one (**7b**) was decomposed thermally in the presence of a copper salt, 2-allylthiolan-3-one (**9b**), b.p. 62°/15 mm, was obtained in 77·5% yield. The pathway for the formation of thiolanone (**9b**) would be [2,3]sigmatropic rearrangement of the ylide (**12b**) generated by the intramolecular electrophilic addition of carbenoid (**11b**) to the sulphur atom, as shown in the Scheme. Photolysis of diazo-ketone (**7b**) in ethanol afforded ethyl 4-allylthiobutyrate in quantitative yield as in the case of (**7a**).

We conclude that in the case of a keto-carbene bearing a sulphide linkage at the δ-position, the photochemically generated free carbene smoothly undergoes Wolff rearrangement to a keten prior to an intramolecular electrophilic attack on the sulphur atom, while the thermally generated

---

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

‡ Evidence for the [2,3]sigmatropic rearrangement of an allylic moiety has been observed in the case of *S*-crotylthietanonium ylide.[3]

copper carbenoid forms the cyclic ylide (**12**), which is stabilized by rearrangement to the thiolanone (**9**). Accordingly, the Wolff rearrangement is effectively suppressed in the latter case.

We thank the Kawakami Memorial Foundation for partial support of this research.

(*Received*, 12*th May* 1972; *Com.* 814.)

---

[1] For example, G. M. Blackburn, W. D. Ollis, L. D. Plackett, C. Smith, and I. O. Sutherland, *Chem. Comm.*, 1968, 186; W. Kirmse and M. Kapps, *Chem. Ber.*, 1968, **101**, 994, 1004; J. E. Baldwin and R. E. Hackler, *J. Amer. Chem. Soc.*, 1969, **91**, 3646; B. M. Trost and R. W. LaRochelle, *ibid.*, 1970, **92**, 5804.

[2] K. Kondo and I. Ojima, *Chem. Letters*, 1972, 119.

[3] K. Kondo and I. Ojima, *J.C.S. Chem. Comm.*, 1972, 62.

[4] W. Kirmse, 'Carbene Chemistry,' 2nd Edn., Academic Press, New York., 1971, pp. 475—492.