appendix to this communication. See paragraph at end of paper regarding supplementary material.

(13) (a) D. M. P. Mingos, W. T. Robinson, and J. A. Ibers, *Inorg. Chem.*, **10**, 1043 (1971); (b) V. G. Albano, P. L. Bellon, and M. Sansoni, *Inorg. Chem.*, **8**, 298 (1969); (c) D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, **8**, 1282 (1969).

(14) D. Forster and G. F. Schaefer, to be submitted for publication, the trans form can be generated by carbonylation of $[Rh(CO)Br_5]^{2-}$. A solution of this trans form in the presence of excess bromine, slowly reverts (over 6 days at 22° and 1 atm of CO) to a mixture of the trans and cis isomers containing ~60% of the trans form. The same position can be reached by adding excess bromines to the *cis*-$Rh(CO)_2Br_2^-$ ion (which immediately generates the *cis*-$Rh(CO)_2Br_4^-$ ion) and allowing this solution to stand for 6 days under 1 atm of CO at 22°. The excess bromine is necessary to prevent decomposition to Rh^I and it is not known at this time whether this excess of bromine affects the equilibrium position in any way. It should be stressed that excess iodine was not present in the solution experiments involving the establishment of the equilibrium position in the $Rh(CO)_2I_4^-$ system.

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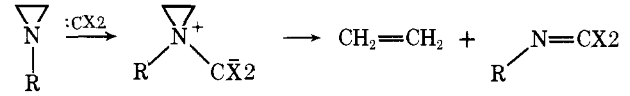
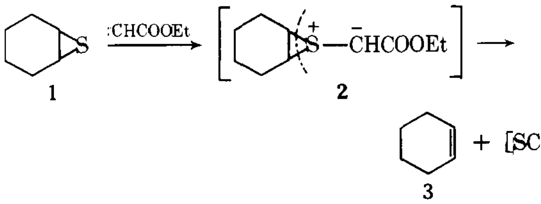
Fragmentation Reaction of Ylides. IV.[1] Reaction of Sulfide and Carbene

Sir:

We previously observed that aziridines react with carbenes to give the corresponding olefins by the simultaneous breaking of two C–N bonds in the aziridine ring.[2] The reactions should be preceded by the initial formation of aziridinium ylide followed by fragmentation of the three-membered ring. This observation was very different from the expected one in the ordinary reactions of ammonium ylide which usually include Stevens rearrangement or degradation into carbene and tertiary amine.[3] We are now interested in extending our research to other hetero three-membered rings. Sulfur compounds especially attract us as they might act to stabilize the ylide by their d-orbital resonance with an anion on an adjacent carbon. We studied the reaction between sulfides and carbenes and report here on the stereospecific fragmentation of *S*-ylide.

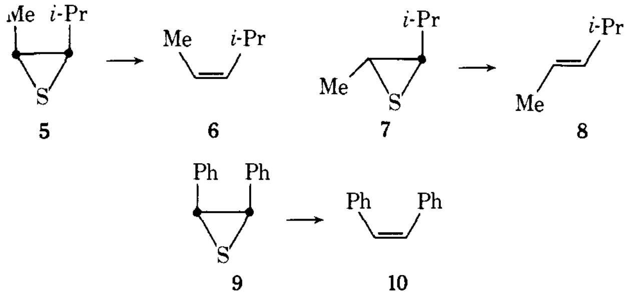


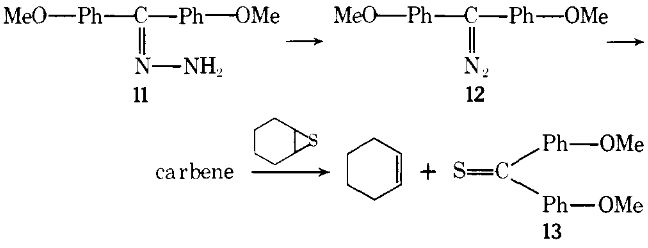
Cyclohexene sulfide and an equimolar amount of ethyl diazoacetate were dissolved in *p*-cymene, and a small amount of $Cu(acac)_2$ was suspended as a catalyst.[4] On heating the solution at 110°, vigorous reaction occurred with the evolution of a gas. After the reaction had ceased, distillation gave 70% cyclohexene. The reaction can be indicated as



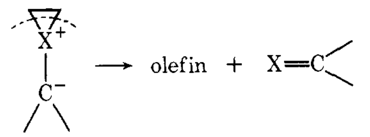
The formation of *S*-ylide from cycloalkyl sulfide and carbene is generally accepted.[5] Episulfide likewise probably formed ylide **2** as an initial intermediate, which then decomposed by fragmentation into cyclohexene and thioglyoxalic ester. The manner of this reaction is the same as that of the reaction of aziridinium ylide. Recently, however, Kondo and his coworkers proposed that the decomposition of alkyl sulfoxide, which is considered to be a kind of ylide, proceeds by stepwise bond cleavage through the formation of a diradical intermediate, and that, as a result, the olefin formed does not retain the stereospecificity of the starting material.[6] This reasoning is contrary to the prediction from the fragmentation of aziridinium ylides. Thus, it seemed of interest to us to examine the stereochemistry of olefin formed from the fragmentation of *S*-ylide, and we carried out the reaction using *cis,trans*-4-methyl-2-pentene sulfide and *cis*-stilbene sulfide.[7]

A mixture of *cis*-4-methyl-2-pentene sulfide (**5**), 2 mol of ethyl diazoacetate, and $Cu(acac)_2$ in ether was heated under reflux for a short time. Olefin isolated at the end of the reaction was examined by VPC. The yield was 72%, and the product was entirely cis isomer **6**, no trans olefin being detectable at all. Thus, the fragmentation of *cis*-4-methyl-2-pentene sulfide ylide proceeded with >99.5% retention of stereochemistry. Another experiment showed that *trans*-4-methyl-2-pentene sulfide (**7**) gave 70% trans olefin **8**, and *cis*-stilbene sulfide (**9**) gave 94% of *cis*-stilbene (**10**) with complete retention of conformation, respectively. Attempts to isolate thioglyoxalic ester, whose formation is predicted by the proposed mechanism, completely failed, perhaps because it is very unstable. However, to understand the reaction, the compound containing the S atom leaving the ylide should be studied. Thus, we next used 4,4′-dimethoxybenzophenone hydrazone (**11**) as the source of carbene. The reaction was carried out using a large excess of cyclohexene sulfide without catalyst or solvent at 50–80°. As the reaction proceeded, the mixture showed the characteristic color of thio ketone **13**, which was isolated at the end of the reaction and identified by uv and ir absorption spectra and by TLC in comparison with an authentic sample. The only olefin produced was cyclohexene.





Nozaki and his coworkers have reported that the reaction of epoxide with carbene also gives olefin, although the yield is poor.[8] Thus, we propose that hetero three-membered ylides have a strong tendency to undergo α-fragmentation as shown in **14**. Four-membered *S*-ylide and four-membered *N*-ylide reportedly give a Stevens rearrangement product but no fragmentation.[2,5] Therefore, α-fragmentation is a



14

X = O, S, N

property exclusive to three-membered ring compounds. The detailed mechanism of the α-fragmentation will be discussed in a full paper in the near future.[9]

Acknowledgment. The authors thank Dr. Y. Onishi of Sagami Chemical Research Center for the supply of 4,4′-dimethoxythiobenzophenone and his valuable discussions.

References and Notes

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(4) Episulfide was stable to Cu(acac)$_2$ without carbene at reaction condition.

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(9) σ-HMO calculation[10] for aziridinium ylide was recently accomplished by Dr. M. Yamakawa of Shionogi Research Lab. In the results, it was indicated that the highest occupied orbital of three-membered C–N bonds was clearly antibonding.

(10) T. Yonezawa, H. Yamabe, and H. Kato, *Bull. Chem. Soc. Jpn.*, **42**, 76 (1969).

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Nucleophilic Substitution at Phosphorus in Tertiary Phosphines. Inversion of Configuration[1]

Sir:

A number of groups have studied nucleophilic substitution at phosphorus[2] in which the phosphorus atom is tetracoordinated (e.g., phosphonium salts,[3] phosphinate esters,[4] and phosphine oxides[5]), tricoordinated,[6] and pentacoordinated.[7] With few exceptions[3b] the stereochemical course of the substitution has been inversion of configuration at phosphorus.[2a,3c,4] Nucleophilic substitution at phosphorus ($\mathrm{SN^P}$) in tertiary phosphines (carbon leaving group) has been mentioned only in passing.[8]

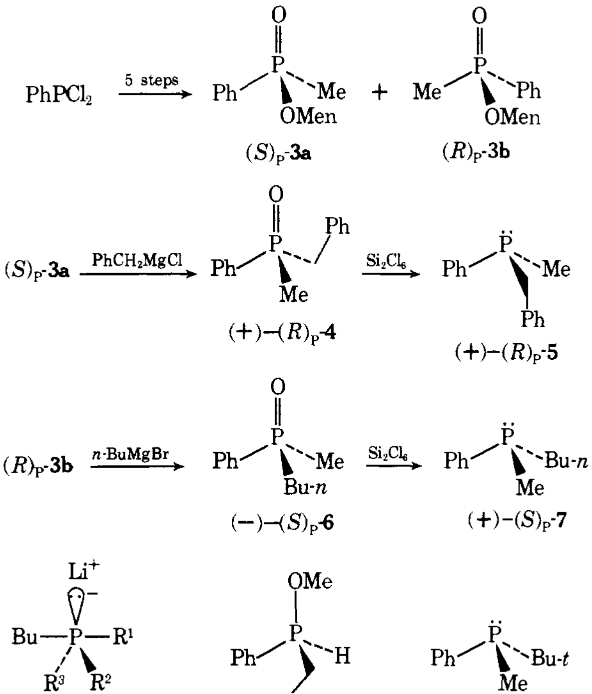
We have recently reported[9] that treatment of tertiary phosphines with alkyllithium reagents, depending upon the medium employed, can lead to $\mathrm{SN^P}$ which is quite competitive with deprotonation (e.g., **1** gives 1.7 times more substitution than deprotonation in THF (eq 1). To our knowledge

$$\underset{\mathbf{1}}{\mathrm{Ph_2PMe}} \xrightarrow[\text{2. } \mathrm{D_2O}]{\text{1. } n\text{-BuLi–THF} \quad 0.5 \text{ hr, room temp}} \underset{19\%}{\mathrm{Ph_2PCH_2D}} + \underset{31\%}{\mathrm{PhP}(n\text{-Bu})\mathrm{Me}} \quad (1)$$

the only study of the stereochemical course of nucleophilic substitution at tricoordinate phosphorus showed that displacement of chloride ion from 1-chloro-2,2,3,4,4-pentamethylphosphetan by methoxide ion and benzylamine occurs with inversion of configuration at phosphorus.[10] The $\mathrm{SN^P}$ process in noncyclic phosphines raised the interesting mechanistic question concerning the nature of the nucleophilic attack on phosphorus. It was conceivable that it could be a direct backside attack ($\mathrm{SN^P2}$, **2** is a transition state), or addition–elimination (**2** is an intermediate), possibly allowing racemization or retention[3b] via pseudorotation, or a frontside attack (known in silicon chemistry[11]). To probe this question we synthesized (+)-$(R)_P$-benzylmethylphenylphosphine (**5**) via the (−)-menthol ester (**3a**)[4a] according to Mislow[12] as outlined in Scheme I. Phosphine **5** ($[\alpha]_D^{25}$ +105° (c 3.00, $C_6H_5CH_3$), lit.[12] $[\alpha]_D$ +81°) was obtained with an enantiomeric excess (ee) ≥95%, as determined by comparison of the NMR spectrum of the phosphonium salt obtained from (+)-**5** and (−)-(R)-1-bromo-2-phenyl-2-methoxyethane (**8**),[4b,13] with that obtained from (±)-**5** and **8**.[14] Phosphine (+)-$(S)_P$-**7** ($[\alpha]_D^{25}$ + 20.3° (c 2.82, C_6H_6)) had 92% ee as determined by the NMR spectra of the phosphonium salts ((+)-**7** + (−)-**8** and (±)-**7** + (−)-**8**).[15] Optically active phosphine **7** has been reported,[16] but no optical rotation data were given. Phosphine (−)-$(S)_P$-**9**[17] was obtained from (+)-$(R)_P$-**5** (vide infra).

Phosphine (+)-$(R)_P$-**5** was subjected to nucleophilic substitution conditions to probe the stereochemistry of the substitution process. Since it was known[9] that the medium can drastically affect the reaction, this was investigated first (Table I). The addition of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) enhances $\mathrm{SN^P}$ in less polar solvents for both nucleophiles. The effect is not nearly as pronounced as with **1** as substrate,[9] however, presumably because benzyl anion is a much better leaving group. The

Scheme I[a]



[a] OMen = (−)-menthoxy.