sorption and emission spectra were obtained on a Beckman Acta III spectrophotometer and an Aminco SPF 500 (corrected spectra) spectrofluorometer, respectively.

***cis*-1,2-Bis(10-acetoxy-9-anthryl)ethylene (2b).** A solution of bis(10-acetoxy-9-anthryl)acetylene (40 mg) in ethyl acetate (200 mL) was hydrogenated under normal conditions over Lindlar catalyst (580 mg). After uptake of 1 molar equiv of hydrogen (1 h), the catalyst was removed by filtration and the solvent was evaporated under reduced pressure. The residue was recrystallized from methylene chloride by addition of cyclohexane to give pale yellow crystals (26 mg, 65%): mp 248–252 °C; ^{1}H NMR (acetone-d_6) δ 8.3 (d, 4 arom H, $J = 9$ Hz), 8.1 (s, 2 H, ethylene H), 7.8 (d, 4 arom H, $J = 9$ Hz), 7.3 (m, 8 arom H), 7.1 (m, 8 arom H), 2.5 (s, 6 H, acetoxy group). The doublets are slightly broadened due to meta coupling. Anal. Calcd for $C_{34}H_{24}O_4$: C, 82.24; H, 4.87. Found: C, 82.02; H, 4.96.

In the ^{1}H NMR spectrum of the trans isomer **1b** in acetone-d_6, the ethylenic protons give rise to a singlet at δ 7.85, and the acetoxy groups give rise to a singlet at δ 2.7. The signals due to the aromatic protons in **1b** appear as three multiplets centered at δ 7.6, 8.15, and 8.7, respectively.

Bis(10-acetoxy-9-anthryl)acetylene (4). A stirred suspension of 1,2-di(10-anthronyl)-1,2-dihydroxyethane (**3**;[10] 2.68 g) in a mixture of pyridine (50 mL) and acetic anhydride (20 mL) was kept at 47 °C for 24 h to give a clear red-brown solution. The reaction mixture was poured into methanol (150 mL) whereupon a red-brown crystalline precipitate formed. The precipitate (1.83 g) consists of a mixture of the acetylene **4** and the previously known (cf. ref 4) dianthronylidenethane (approximate ratio 1:1). Separation of the two products was accomplished by column chromatography (SiO_2/CH_2Cl_2). The yield of **4** (orange-red crystals of low solubility, mp 289–295 °C) was 30% based on **3**: ^{1}H NMR ($CDCl_3$) δ 8.9 (d, 4 H, $J = 8$ Hz), 8.05 (d, 4 H, $J = 8$ Hz), 7.6 (m, 8 H) [meta coupling ($J = 1$ Hz) detectable for all four types of aromatic protons], 2.69 (s, 6 H, acetoxy group). Anal. Calcd for $C_{34}H_{22}O_4$: C, 82.58; H, 4.48. Found: C, 82.33; H, 4.46.

Photochemical Experiments. Quantum yields of emission are based on the fluorescence quantum yield of 9,10-diphenylanthracene ($\Phi = 0.83$).[12] The photochemical isomerization of **2b** into **1b** was brought about by irradiating a 3×10^{-4} M solution in cyclohexane, using light of 366-nm wavelength. The formation of **1b** was monitored by measuring the increase of absorption at 450 nm in conjunction with the decrease of the **2b** absorption around 370 nm. For the determination of the quantum yield of isomerization, the intramolecular photochemical cycloadditon of 1,2-di(9-anthryl)ethane ($\Phi = 0.26$)[13] was used in the actinometric experiment.

Acknowledgment. We are indebted to Professor Ernst Fischer, Rehovot, Israel, for a stimulating discussion and for helpful comments regarding the manuscript.

Registry No. 1b, 75919-24-3; **2b**, 75919-25-4; **3**, 75919-26-5; **4**, 75919-27-6; 1,2-bis(10-acetoxy-9-anthryl)ethane, 58382-04-0.

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(12) Birks, J. B. "Photophysics of Aromatic Molecules"; Wiley-Interscience: New York, 1970; p 317.

(13) Livingston, R.; Wei, K. S. *J. Am. Chem. Soc.* **1967**, *89*, 3098.

Unsaturated Carbenes. 14. Divinyl Sulfides via Insertion of Isopropylidenecarbene into Enethiols[1]

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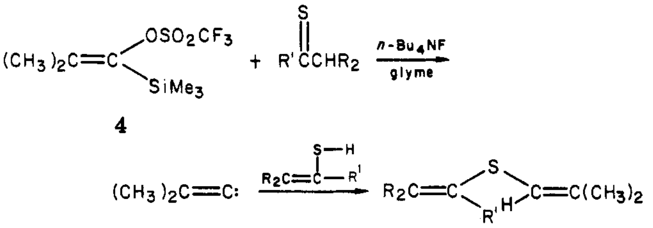
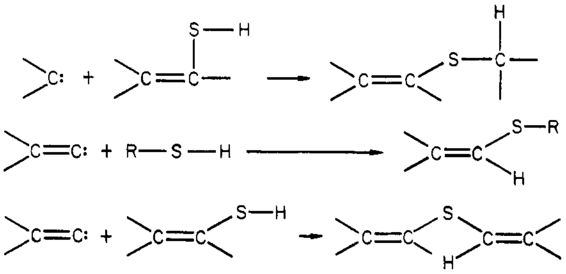
Carbene insertions into X–H bonds such as C–H, Si–H, O–H, and others are well-known and in many instances result in synthetically useful products.[2] Similarly, unsaturated carbenes readily insert into Si–H, O–H, and N–H bonds.[3] Little is known, however, about the insertion of either species into S–H bonds and in particular the S–H of enethiols.[4] Insertion of carbenes into enethiols or of unsaturated carbenes into alkyl thiols would result in alkyl vinyl sulfides, whereas interaction of unsaturated carbenes with enethiols should give divinyl sulfides. Although dialkyl and alkyl vinyl sulfides are well-established compounds, little is known about divinyl sulfides.[5] Hence in this note we report the formation of divinyl sulfides by the interaction of isopropylidenecarbene with several thiones.

Scheme I





Dialkyl thiones **1–3** were prepared from the corresponding commercially available carbonyls by standard procedures.[6] As these thiones react with strong bases, such as *t*-BuOK, the carbene was generated[7] from silylvinyl triflate **4** with tetrabutylammonium fluoride as shown in Scheme I.

Interaction of the thione, dissolved in glyme at −23 °C, with a 10% molar excess of triflate **4** gave, upon addition of R_4NF, divinyl sulfides **5–7** in 25–40% yield. The products were isolated by medium-pressure LC and characterized by spectral means as summarized in Table I. The spectral data are in complete accord with the proposed structures.

It is well-known that the ene thiol content of these dialkyl thiones is in the 20–40% range.[6] Furthermore, unlike carbonyls, the thione $\rightleftarrows$ enethiol tautomerization is believed to be very slow, with separation and isolation of the individual tautomers possible.[6] Since we made no attempt to separate the tautomers, the formation of divinyl sulfides **5–7** may actually be quantitative, based on the enethiols consumed. In conclusion, interaction of unsaturated carbenes with thiocarbonyls provides a simple, general means of preparing pure divinyl sulfides, albeit in only modest isolated yields.

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(1) Paper 13: Stang, P. J.; Fisk, T. E. *J. Am. Chem. Soc.* **1980**, *102*, 6813.

(2) Hine, J. "Divalent Carbon"; Ronald Press: New York, 1964. Kirmse, W. "Carbene Chemistry", 2nd ed.; Academic Press: New York, 1971. Jones, M., Jr.; Moss, R. A. "Carbenes"; Wiley-Interscience: New York, 1973, Vol. 1; 1975, Vol. 2.

(3) Stang, P. J. *Chem. Rev.* **1978**, *78*, 383.

(4) We are not aware of the interaction of *any* free carbenes with thiocarbonyls. The addition of diazoalkanes to thiones has been extensively investigated: Beiner, J. A. et al. *Bull. Soc. Chim. Fr.* **1973**, 1979–1983; Pagner, D.; Vialle, J. *Ibid.* **1969**, 3327; Clinet, J.-C.; Julia, S. *J. Chem. Res. (M)* **1978**, 1714–1726.

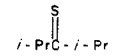
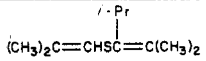
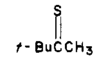
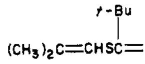
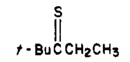
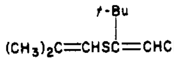
(5) Stirling, C. J. M., Ed. "Organic Sulphur Chemistry"; Butterworths: London, 1975.

(6) Pagner, D.; Vialle, J. *Bull. Soc. Chim. Fr.* **1969**, 3595.

(7) Stang, P. J.; Fox, D. P. *J. Org. Chem.* **1977**, *42*, 1667.

0022-3263/81/1946-0823$01.00/0

Table I. Yields and Spectral Properties of Divinyl Sulfides

starting thione	product sulfide	% yield[a]	mass spectrum, *m/e* (relative intensity)	IR,[b] cm^{-1}	NMR,[c] δ
 $i\text{-PrC}(=S)\text{-}i\text{-Pr}$ **1**	 $(CH_3)_2C{=}CHSC(i\text{-Pr}){=}C(CH_3)_2$ **5**	40	186 (M$^+$ + 2, 7.7), 185 (M$^+$ + 1, 12.4), 184 (M$^+$, 69), 141 (15), 97 (63), 55 (100)	1620 (C=C)	1.05 (d, *J* = 7, 6, *i*-Pr), 1.75 (s, 3, CH$_3$), 1.77 (s, 3, CH$_3$), 1.85 (s, 3, CH$_3$), 1.95 (s, 3, CH$_3$), 3.10 (sept, 1, CH), 5.45 (m, 1, C=CH)
 $t\text{-BuC}(=S)CH_3$ **2**	 $(CH_3)_2C{=}CHSC(t\text{-Bu}){=}CH_2$ **6**	31	172 (M$^+$ + 2, 4.9), 171 (M$^+$ + 1, 11.8), 170 (M$^+$, 77), 113 (76), 101 (90), 57 (100)	1600 (C=C)	1.20 (s, 9, *t*-Bu), 1.80 (br s, 3, CH$_3$), 1.90 (br s, 3, CH$_3$), 4.75 (s, 1), 5.15 (s, 1), 5.80 (m, 1)
 $t\text{-BuC}(=S)CH_2CH_3$ **3**	 $(CH_3)_2C{=}CHSC(t\text{-Bu}){=}CHCH_3$ **7**	26	186 (M$^+$ + 2, 5.7), 185 (M$^+$ + 1, 13.1), 184 (M$^+$, 75), 127 (71), 55 (100)	1620 (C=C)	1.15 (s, 9, *t*-Bu), 1.75 (m, 6), 1.76 (d, *J* = 6, 3), 5.25 (m, 1), 5.85 (q, *J* = 6, 1)

[a] Isolated yield, based on total thione used; see text. [b] Neat, NaCl plates. [c] In CCl$_4$, internal Me$_4$Si.

Experimental Section

Infrared spectra were recorded on a Beckman IR5A spectrometer, and proton NMR spectra were recorded on a Varian EM-390 spectrometer. Mass spectra were obtained on a Varian MAT 112 GC-mass spectrometer. All commercial reagents were ACS reagent grade and solvents were purified and dried prior to use.

Thiones 1-3 were prepared by reaction of the corresponding commercial carbonyls with liquid H_2S and gaseous HCl according to literature procedures.[6] Vinyl triflate 4 and tetra-*n*-butylammonium fluoride were prepared as previously reported.[7]

Reaction of Vinyl Triflate 4 with Diisopropyl Thioketone. Formation of Divinyl Sulfide 5. General Procedure. To a flame-dried 100-mL round-bottom flask, equipped with a serum cap, magnetic stirring bar, and an argon inlet and outlet via syringe needles, were added 0.65 g (5 mmol) of diisopropyl thioketone, 1.38 g (5.5 mmol) of silylvinyl triflate 4 and 50 mL of dry glyme. The solution was cooled to −23 °C with a dry ice-CCl_4 slush bath. To the cooled solution was added, all at once via a syringe, 7 mL of a 0.81 M (5.67 mmol) solution of *n*-Bu_4NF in glyme. The red-orange color of the solution rapidly faded to pale yellow. The solution was stirred at −23 °C for 1 h. At the end of this period the solvent was removed under reduced pressure and the residue was taken up in pentane. The pentane solution was filtered to remove the salts and then concentrated and subjected to medium-pressure LC with a silica gel column. Elution with hexanes gave the product in the lead fraction. Evaporation of the solvent yielded 367 mg (40%) of divinyl sulfide 5 as a colorless liquid.

Acknowledgment. This investigation was supported by Public Health Service Research Grant CA16903-04 from the National Cancer Institute.

Registry No. 1, 13390-86-8; 2, 17380-91-5; 3, 25946-21-8; 4, 73876-87-6; 5, 75961-70-5; 6, 75961-71-6; 7, 75961-72-7.

Improvements in the Hexachloroacetone/Triphenylphosphine Procedure for the Conversion of Allylic Alcohols into Chlorides

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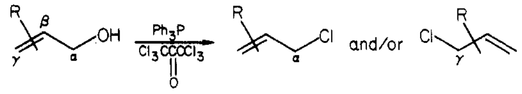
Several procedures have been described for the conversion of allylic alcohols into chlorides with predictable stereo- and regiochemistry, but none is generally applicable to all types of substitution patterns.[2] Recently we reported[3] that the reagent system hexachloroacetone (HCA)/triphenylphosphine provides a partial solution to this synthetic problem: primary and secondary allylic alcohols afford nearly quantitative yields of largely or exclusively unrearranged chloride; the geometry of the β-γ double bond is preserved; inversion of configuration occurs at C$_\alpha$; the conditions of the reaction, workup, and isolation are exceedingly mild.



Two drawbacks of the procedure are the wasteful use of HCA as solvent as well as reagent and the extensive rearrangement and elimination which occur with tertiary allylic alcohols. We sought a solvent which would address the first problem and, perhaps, alleviate the second. Criteria for selection of a solvent include the following: high boiling point (to allow easy isolation of volatile allylic chlorides); high polarity; inertness to HCA, Ph_3P, and the allylic alcohol. Of the several dipolar aprotic solvents tested, we are pleased to report that sulfolane (tetramethylene sulfone) is a superior medium for this synthesis: reaction occurs rapidly under mild conditions, yields are high, and isolation of the chloride is facile.

Our initial studies were with β-methylallyl alcohol (2-methyl-2-propen-1-ol, 1), a symmetrical molecule (in the absence of an isotopic label) which does not produce a mixture of regioisomers. As shown in Table I, Ph_3P, alcohol 1, and a stoichiometric quantity of HCA in sulfolane give an excellent yield of chloride regardless of the order of mixing of the reagents (runs 3-5). For all of the entries (except runs 4 and 5) HCA in sulfolane was added to a stirred, cooled mixture of the alcohol and triphenylphosphine in the same solvent. Excess HCA (runs 1 and 2) is not beneficial in terms of yield or rate. Significantly, the yield of allylic chloride is not appreciably diminished when even as little as 0.4 equiv of HCA is used (runs 6-9). This suggests that two chlorines are available from HCA, support for which comes from the observation of singlets at δ 6.8 and 6.5, respectively, for pentachloroacetone and *sym*-tetrachloroacetone in the residue from flash distillation; under the conditions of short reaction time and low temperature, more than two chlorines are not used (runs 10 and 11). That the isolated yield of allylic chloride is not even higher is attributed, in part, to its high volatility. Another noteworthy feature is that the persistent forma-

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(1) National Science Foundation Undergraduate Research Participant, summer 1980.

(2) R. M. Magid, *Tetrahedron*, **36**, 1901 (1980).