(32.4 mmol) of triphenylphosphine, and 2 ml of anhydrous methylene chloride was placed in a Carius tube which was then sealed under nitrogen and heated to 105° for 4.5 hr (no reaction occurred at room temperature over a period of 3 weeks). The infrared spectrum of the crude product indicated the absence of triphenylarsine oxide (within detectability by this method). Chromatography over Florisil and elution with benzene gave 0.92 g (93%) of triphenylarsine, mp 60–61°, undepressed by admixture of an authentic sample; the product was also identified by its infrared spectrum. Elution with methylene chloride–tetrahydrofuran (7:3) gave 0.81 g (86%) of triphenylphosphine oxide which was identified by comparison of its infrared spectrum with that of an authentic sample. Elution with tetrahydrofuran–methanol (9:1) gave 0.05 g of triphenylarsine oxide hydrate as indicated by its infrared spectrum.

Registry No.—Triphenylphosphine oxide, 791-28-6; triphenylarsine oxide, 1153-05-5; **1**, 23853-23-8; **4a**, 23853-24-9; **4b**, 23853-25-0; **5**, 23853-26-1; **10a**, 23853-27-2; **10b**, 23853-28-3; **10c**, 23853-29-4; **10d**, 23853-30-7; **10e**, 23853-31-8; methyl 12-cyano-9,10-dihydro-9,10-ethenoanthracene-11-carboxylate, 23853-32-9.

Adducts of Acetylenes and Sulfur Dichloride

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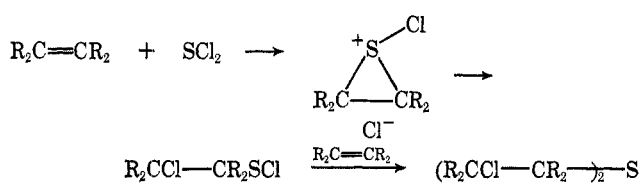
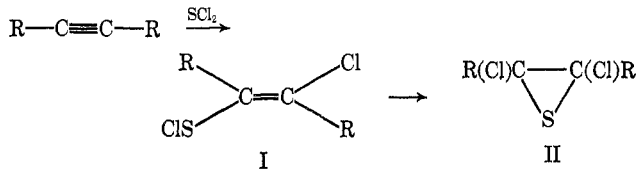
Reactions of selected acetylenes with sulfur dichloride have been studied. Dialkylacetylenes afford the corresponding divinyl sulfides (III) in quantitative yield. Diphenylacetylene provides either 3-chloro-2-phenylbenzo[*b*]thiophene (IV) or the divinyl sulfide VIII, depending upon the reaction conditions. In certain cases it is possible to isolate in good yield the intermediate vinylsulfenyl chloride, which can be utilized in a variety of synthetic schemes. The stereochemistry of the acetylene adducts is *trans*. Orientation of addition to unsymmetrical acetylenes is largely anti-Markovnikov. This orientation has been found to be relatively insensitive to the nature of the solvent. The relative reactivity of sulfur dichloride to olefins and acetylenes follows the usual order of electrophiles except with *trans*-stilbene, which was always the least reactive member in competition experiments.

Interest in the organic chemistry of sulfur dichloride has recently been revived and has led to the syntheses of a number of novel sulfur-containing heterocycles.[1-5] However, the investigations of interactions with multiple bonds to date have been largely limited to reactions of sulfur dichloride and olefins. Surprisingly, no report of a reaction of sulfur dichloride with an acetylene has appeared in the literature. We present here the results of the addition of this versatile reagent to diaryl-, arylalkyl-, and dialkylacetylenes.

From the products (and most importantly their stereochemistry) resulting from reaction of sulfur dichloride and olefinic systems, it has been concluded[1-5] that the mechanistic course of this reaction is the initial formation of an episulfonium ion, which is then opened to an alkylsulfenyl chloride. This latter species may then proceed to products by reaction with another olefinic bond.



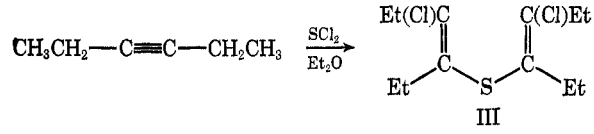
The analogous reaction with alkynes is more difficult to predict, especially in view of the uncertainty of the stereochemistry of electrophilic addition to triply bonded species.[6] However, it has been shown by a number of workers that the addition of sulfenyl halides to alkynes proceeds so as to afford *trans* products almost exclusively.[7-9] Initially it was hoped by us that the final product of this reaction would be a thiirane, thus providing a simple route to this sometimes elusive ring system. By analogy to the reactions of sulfur dichloride with olefins and the reactions of other electrophiles, such as bromine, with acetylenes the initial adduct would be expected to be a vinylsulfenyl chloride (I). Ring closure resulting from internal attack of the sulfenyl chloride upon the adjacent double bond could then provide the thiirane (II).



I II

Results and Discussion

The first acetylene examined in our study was the readily available 3-hexyne. Addition of freshly distilled sulfur dichloride to an ethereal solution of 3-hexyne afforded the divinyl sulfide (III) as a colorless



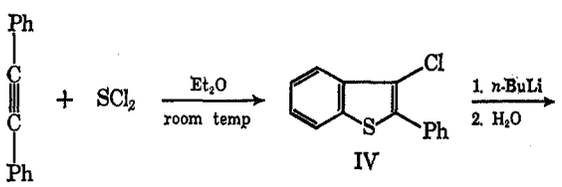
III

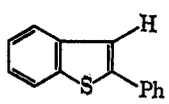
liquid in 95% yield. The structure assigned was founded on the mass spectrum (base and parent peak *m/e* 266), elemental analysis, the nmr spectrum (showing only two nonequivalent ethyl groups), and conversion

(1) E. J. Corey and E. Block, *J. Org. Chem.*, **31**, 1663 (1966).
(2) E. D. Weil, K. J. Smith, and R. J. Gruber, *ibid.*, **31**, 1669 (1966).
(3) F. Lautenschlaeger, *ibid.*, **31**, 1679 (1966).
(4) F. Lautenschlaeger, *Can. J. Chem.*, **44**, 2813 (1966).
(5) F. Lautenschlaeger, *J. Org. Chem.*, **33**, 2620, 2627 (1968).
(6) T. C. Fahey and D. J. Lee, *J. Amer. Chem. Soc.*, **88**, 5555 (1966), and references cited therein.
(7) A. Dondoni, G. Modena, and G. Scorrano, *Boll. Sci. Fac. Chim. Ind. Bologna*, **22**, 26 (1964).
(8) V. Caló, G. Melloni, G. Modena, and G. Scorrano, *Tetrahedron Lett.*, No. 49, 4399 (1965).
(9) L. DiNunno, G. Gelloni, G. Modena, and G. Scorrano, *ibid.*, No. 49, 4405 (1965).

of the corresponding sulfone into propionic acid *via* ozonolysis. Inversion of the addition procedure, changes in dilution factors, and temperature changes failed to affect the nature or yield of product. No evidence of the presence of a dichlorothiirane could be found.

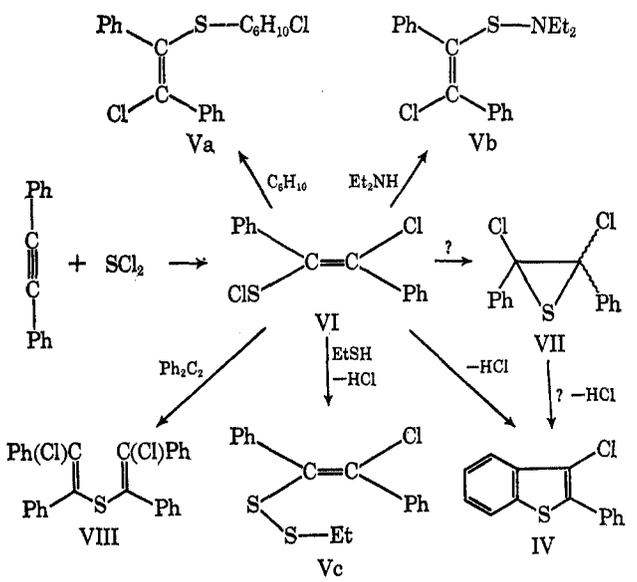
A dramatically different result was obtained when this reaction was attempted with a diarylacetylene. Dropwise addition of an equimolar solution of sulfur dichloride in dry ether to an ether solution of diphenylacetylene at room temperature led to isolation of a bright yellow solid after solvent removal *in vacuo*. Upon standing at room temperature this material lost most of its color, with concomitant hydrogen chloride loss, to provide a white solid (IV). This same conversion could be quantitatively performed by washing a methylene chloride solution of the product with aqueous sodium bicarbonate. Owing to the extreme instability of the initial product, spectral observations were always made on mixtures; however, the mass spectrum clearly showed that it was a 1:1 adduct of diphenylacetylene and sulfur dichloride which lost the elements of SCl_2 in stepwise processes to return to diphenylacetylene. The structure of the ultimate, colorless product was assigned as 3-chloro-2-phenylbenzo[*b*]thiophene (IV) on the basis of melting point (lit.[10] mp 67–68°), mass spectrum (parent ion *m/e* 244 with proper isotopic ratios for SCl), elemental analysis, and conversion into the known 2-phenylbenzo[*b*]thiophene[11] by dechlorination with *n*-butyllithium. 3-Chloro-2-phenylbenzo[*b*]thiophene (IV) was obtained from diphenylacetylene in this manner in yields up to 90%.



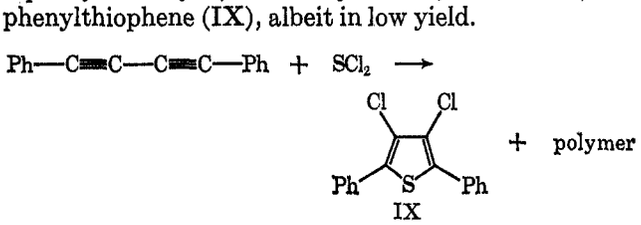


One question with which we were confronted at this point was whether IV arose from initial formation of the vinylsulfenyl chloride VI followed by electrophilic attack by sulfur on the adjacent aromatic ring or whether it was a thermolysis product of the diphenyldichlorothiirane VII. Certainly the latter-named process would appear an unnecessary consideration except that analogy for the conversion of VII into IV is found in the known thermal conversions of several α-chloroepisulfides to benzo[*b*]thiophenes by both Staudinger[12] and Schönberg.[13]

Evidence that VI was the intermediate with which we were dealing was easily obtained. A number of derivatives of VI were prepared through reaction with mercaptans, secondary amines, and olefins, thus further confirming its structure. The synthetic possibilities of being able to stop this reaction at the 1:1 adduct stage are therefore numerous and quite attractive. When the sulfur dichloride–diphenylacetylene reaction was run as before, but with methylene chloride as the solvent, no IV was obtained but high yields of the divinyl sulfide VIII were afforded. Compound VIII was also the sole product when 2 equiv of diphenylacetylene were employed. It was at first presumed that this product change in going to methylene chloride must be solely due to a change in solvent polarity; however, when the reaction was accomplished in either hexane or acetonitrile, the divinyl sulfide VIII was again the only product isolated. While the unique role of ether is not presently understood, it is true that by varying the reaction conditions either product, and mixtures of the two, may be obtained from all of these solvents. Presumably, ether solvates and stabilizes in some fashion the intermediate sulfenyl chloride so as to make the intermolecular process less favorable.



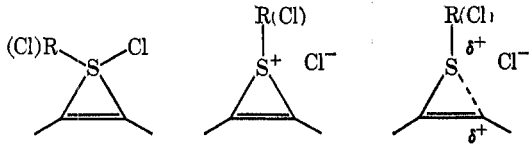
Another illustration of the synthetic utility of the sulfur dichloride–acetylene system is the reaction with diphenylbutadiyne, which yields 3,4-dichloro-2,5-diphenylthiophene (IX), albeit in low yield.



Concerning the mode of addition of sulfur dichloride to alkynes, one must first consider similar work which has been reported for alkyl- and arylsulfenyl chlorides. First, although the investigations of Fahey[6] have shown that addition of protonic acids to alkynes may proceed either in a *cis* or *trans* fashion, additions of sulfenyl chlorides have been found to proceed solely or almost exclusively in a *trans* fashion.[7,8,14–16] It might be assumed that in the case of arylacetylenes the reaction would proceed in a Markovnikov fashion, but the orientation has been found to be highly solvent de-

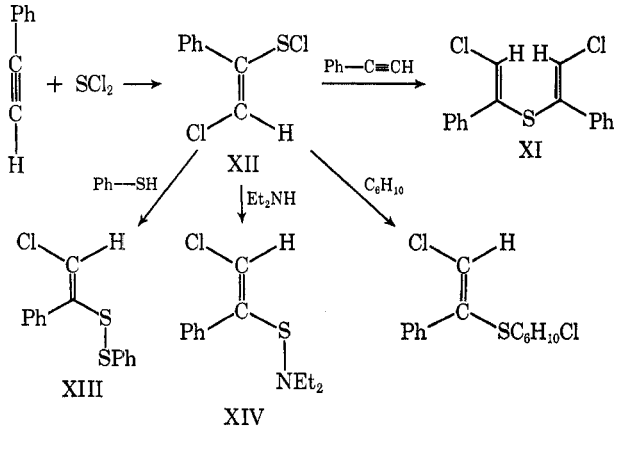
(10) E. J. Geering, U. S. Patent 3,278,552 (1966).
(11) M. G. Voronkov and V. Udre, *Khim. Geterotsikl. Soedin.*, **4**, 527 (1966); *Chem. Abstr.*, **66**, 65344 (1967). G. M. Badger, N. Kowanko, and W. H. F. Sasse, *J. Chem. Soc.*, 2969 (1960).
(12) H. Staudinger and J. Siegwart, *Helv. Chim. Acta*, **3**, 840 (1920).
(13) A. Schönberg and L. Varga, *Ann. Chem.*, **483**, 176 (1930).
(14) V. Caló, G. Modena, and G. Scorrano, *J. Chem. Soc., C*, 1339 (1968).
(15) G. H. Schmidt and M. Heinola, *Quart. Rep. Sulfur Chem.*, **2**, 311 (1967).
(16) V. Caló, G. Scorrano, and G. Modena, *J. Org. Chem.*, **34**, 2020 (1969).

pendent. A strong preference for Markovnikov orientation is observed only in highly polar solvents (*e.g.*, acetic acid) while less polar solvents (*e.g.*, ethyl acetate) afford mainly anti-Markovnikov products. Such results are most easily explained by the assumption of an initial complex which may be either covalent (Xa) or ion paired (Xb). The nature of this intermediate would depend upon the ion-stabilizing characteristics of the solvent. With a single electron-donating substituent on the reacting acetylene and an ionizing solvent, the intermediate could take on much of the character of Xc. Therefore the observation of a predominance of anti-Markovnikov products in solvents of low polarity can be simply explained on the basis of steric crowding in the transition state for nucleophilic attack by chloride ion. Similar conclusions have been recently reached by Modena.[16]



Xa Xb Xc

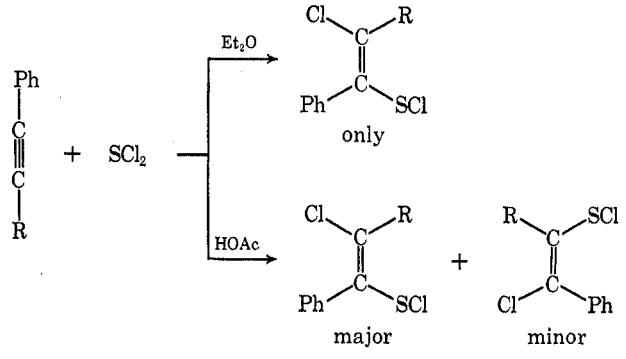
With diphenylacetylene the addition of sulfur dichloride is occurring in a *trans* fashion, since the resulting vinylsulfenyl chloride is able to cyclize to a benzo[*b*]thiophene. To obtain situations where there would be a possibility for both Markovnikov and anti-Markovnikov addition, two unsymmetrical acetylenes were studied. Reaction of 2 equiv of phenylacetylene with sulfur dichloride in ether or methylene chloride provided the divinyl sulfide XI, while equimolar amounts yielded the vinylsulfenyl chloride XII. The latter material was remarkably stable and could be purified by distillation. Derivatives of XII were prepared through reaction with olefins, secondary amines, and mercaptans.



XIII XIV

The stereochemistry of XII is assumed to be *trans* as is the case with diphenylacetylene. If the addition had taken place in a Markovnikov fashion the resulting sulfenyl halide would be expected to form 3-chlorobenzo[*b*]thiophene but this product was not observed. Changing the solvent to acetic acid would be expected to provide a considerable amount of the Markovnikov product and ultimately the benzo[*b*]thiophene. The results were much less dramatic than expected and a maximum yield of *ca.* 16% 3-chlorobenzo[*b*]thiophene (determined from the nmr spectrum of the crude reaction mixture) could be obtained.

Similar results were found for 1-phenylpropyne. In solvents of low polarity, the vinylsulfenyl chloride was produced with only minor contamination by the divinyl sulfide when equimolar amounts of the two reactants were employed. Use of acetic acid as the solvent medium provided no more than 20% of the benzo[*b*]-thiophene product. It is therefore quite clear that steric effects on the nucleophilic addition of chloride anion play the largest role regardless of the solvent nature. This situation has been most conclusively established in the case of sulfenyl halide addition to olefins.[17]



(R = H, CH_3)

An interesting feature of the reaction of sulfur dichloride with acetylenes to afford divinylacetylenes is that both sulfur dichloride and the vinylsulfenyl chloride prefer to attack an acetylene molecule rather than either another vinylsulfenyl chloride or the product divinyl sulfide. It has been conclusively shown that olefins are more reactive to sulfenyl halides than are alkynes.[18] Even with strongly electron-withdrawing groups attached to the sulfenyl chloride there is still a significant difference in the reaction rates of these two multiple bonds. Presumably our observations on olefin–acetylene reactivity result from the decreased π-electron density of the olefin products which are substituted with electronegative groups. In a qualitative fashion we set out to check this assumption through a series of competition experiments. When 0.5 equiv of sulfur dichloride was slowly added to an equimolar solution of cyclohexene and diphenylacetylene, immediate examination of the resulting mixture by nmr revealed that the products were almost exclusively those derived from cyclohexene. However, when a similar competition was performed between the more comparable *trans*-stilbene and diphenylacetylene, only products derived from diphenylacetylene were afforded. This latter result was totally unexpected, especially in view of the observations by Kharasch[18] that stilbene was more reactive to 2,4-dinitrobenzenesulfenyl chloride than was diphenylacetylene and by Robertson[19] that stilbene was some 250 times more reactive toward bromine than was diphenylacetylene. Similar results were obtained when phenylacetylene replaced diphenylacetylene in these experiments. To determine the role of the aryl groups, the same competitions were examined

(17) W. H. Mueller and P. E. Butler, *J. Amer. Chem. Soc.*, **90**, 2075 (1968).

(18) N. Kharasch and C. N. Yiannios, *J. Org. Chem.*, **29**, 1190 (1964).

(19) P. W. Robertson, W. E. Dasent, R. M. Milburn, and W. H. Oliver, *J. Chem. Soc.*, 1628 (1950).

with 2-butyne as the acetylenic member. All olefins examined in our laboratory to date have proved to be considerably more reactive to SCl_2 than the acetylenes employed with the glaring and consistent exception of *trans*-stilbene. The factors involved in this inconsistency are presently under active investigation in our laboratory.

Experimental Section

Melting points and boiling points are uncorrected. Microanalyses were performed by Ilse Beetz Mikroanalytisches Laboratorium, Kronach, West Germany. The nmr spectra were recorded on a Varian A-60 instrument; chemical shifts are measured in parts per million downfield from tetramethylsilane. The mass spectra were measured with a Atlas CH-4 mass spectrometer. Commercial sulfur dichloride (Matheson Coleman and Bell) was purified by vacuum distillation to remove chlorine, followed by two distillations at atmospheric pressure using equipment previously washed with a dilute solution of PCl_3 in methylene chloride.

Bis-4-chlorohex-3-en-2-yl Sulfide (III).—To a stirred solution of 8.21 g (0.10 mol) of 3-hexyne in 15 ml of dry ether was added dropwise a solution of 6.18 g (0.06 mol) of freshly distilled sulfur dichloride in 5 ml of dry ether. The temperature of the reaction was maintained at 0° and the addition required 45 min. Evaporation of the solvent and distillation of the liquid residue gave 12.7 g of a yellow liquid, bp 75–95° (0.3 mm). Redistillation using a Vigreux column afforded 12.30 g (92%) of colorless III: bp 92–93° (1.1 mm); the nmr spectrum showed only two nonequivalent ethyl groups; mass spectrum *m/e* 268 (69% of 266 peak, therefore the p + 2 peak for the parent ion containing SCl_2), 266 (p), 231 (p − Cl), 149 (p − $C_6H_{10}Cl$, S–C cleavage), and 115 (base peak).

Anal. Calcd for $C_{12}H_{20}Cl_2S$: C, 53.93; H, 7.54; S, 12.00. Found: C, 54.27; H, 7.58; S, 12.17.

3-Chloro-2-phenylbenzo[*b*]thiophene (IV).—A solution of 1.03 g (0.01 mol) of sulfur dichloride in 10 ml of dry ether was added dropwise at room temperature to a stirred solution of 1.78 g (0.01 mol) of diphenylacetylene in 20 ml of dry ether. Solvent removal *in vacuo* afforded a bright yellow, crystalline solid which readily lost hydrogen chloride to give near quantitative yields of IV. Conversion into IV was also accomplished by dissolving 0.3 g of the yellow solid VI in 15 ml of methylene chloride and washing with 25 ml of 2% sodium bicarbonate solution in a separatory funnel. The aqueous layer was separated and extracted twice with 20 ml of methylene chloride. The combined methylene chloride solutions were dried over magnesium sulfate and the solvent was evaporated to afford an oily residue. Crystallization from methanol gave 0.19 g (75%) of white, crystalline IV: mp 67° (lit.[10] mp 66–67°); mass spectrum *m/e* 246 (38% of 246 peak, therefore the p + 2 peak for the parent ion containing SCl), 244 (parent ion and base peak), 208 (−HCl), 165, 122 (p^{2+}), and 104.

Anal. Calcd for $C_{14}H_9SCl$: C, 68.71; H, 3.71; S, 13.10; Cl, 14.49. Found: C, 68.32; H, 3.66; S, 12.94; Cl, 14.51.

2-Phenylbenzo[*b*]thiophene.—To a stirred solution of 1.000 g (4.1 mmol) of IV in 15 ml of dry ether under N_2 was added 0.262 g (4.1 mmol) of *n*-butyllithium. The reaction was exothermic and an orange-brown color was generated. After stirring for 15 min at room temperature and refluxing for an additional 5 min, the reaction was decomposed with dilute HCl. The aqueous layer was separated and washed with three 20-ml portions of methylene chloride. The combined organic layers were dried over magnesium sulfate. Evaporation of the solvent left a yellow, crystalline solid which was recrystallized from methylene chloride–ether to afford 0.10 g (12%) of white, crystalline 2-phenylbenzo[*b*]thiophene, mp 172–173° (lit.[11] mp 176°).

Anal. Calcd for $C_{14}H_{10}S$: C, 79.96; H, 4.79; S, 15.25. Found: C, 80.23; H, 4.71; S, 15.25.

2-Chloro-1,2-diphenylethenesulfenyl Chloride, (*E*)-VI.—A solution containing 6.00 g (33.7 mmol) of diphenylacetylene in 100 ml of dry ether was added during 1.5 hr to a stirred solution of 3.47 g (33.7 mmol) of freshly distilled sulfur dichloride in 200 ml of refluxing dry ether, and 50-ml aliquots of the resulting orange solution containing 1.58 g (5.61 mmol) of VI were used in the following procedures.

A. Cyclohexyl-2-chloro-1,2-diphenylethen-1-yl Sulfide (Va).—The 50-ml aliquot of VI was added to a solution containing a slight molar excess of cyclohexene in dry ether. After stirring for 30 min the solvents were removed *in vacuo* to afford a yellow oil. Crystallization from ether–methanol gave 1.00 g (49%) of white, crystalline Va: mp 91–92°; nmr (CCl_4) 1.59 (m, 8, methylene H), 2.57 (m, 1, HCS), 3.83 (m, 1, HCCl), and 7.40 (m, 10, ArH); mass spectrum *m/e* 362 (parent), 210 (base peak, p − $C_6H_{10}Cl$), and 178 (p − $C_6H_{10}SCl_2$).

B. Bis-2-chloro-1,2-diphenylethenyl Sulfide, (*E*)-VIII.—The 50-ml aliquot of VI was added to a solution of 1.00 g (56 mmol) of diphenylacetylene in 25 ml of ether. After stirring for 30 min the ether was evaporated to leave a pale yellow solid. Crystallization from methylene chloride–hexane gave a quantitative yield of VIII. Further recrystallization from chloroform–hexane gave colorless needles, mp 151–152°.

An alternate preparation of VIII involved addition of an equimolar amount of sulfur dichloride in methylene chloride to an ice-cooled, room temperature or refluxing solution of diphenylacetylene in methylene chloride. The conditions were the same as for the preparation of IV. However, removal of solvent *in vacuo* followed by crystallization from methanol provided a 70% yield of VIII: mp 152.0–152.5°; nmr (CCl_4) 7.33 (m); mass spectrum *m/e* 460 (68% of 458 peak, p + 2), 458 (parent ion), 423 (p − Cl), 388 (p − Cl_2), 356 (M* for 423 → 388), 210 (p − $Ph_2C_2Cl_2$), and 178 (base peak, Ph_2C_2).

Anal. Calcd for $C_{28}H_{20}SCl_2$: C, 73.20; H, 4.39; S, 6.98; Cl, 15.43. Found: C, 73.04; H, 4.28; S, 6.97; Cl, 15.66.

C. Ethyl 2-Chloro-1,2-diphenylethen-1-yl Disulfide (Vc).—The 50-ml aliquot of VI was added to a solution of excess ethyl mercaptan in 25 ml of dry ether. After stirring for 30 min the solvent was evaporated and the resulting yellow oil crystallized from ether–methanol to afford 0.037 g of white, cottonlike Vc: mp 57–58°; nmr ($CDCl_3$) 0.97 (t, 3, methyl H), 2.20 (q, 2, methylene H), and 7.43 (m, 10, ArH); mass spectrum *m/e* 306 (parent ion) and 210 (base peak, *p* − EtSCl).

D. N,N-Diethyl 2-chloro-1,2-diphenylethen-1-yl Sulfenamide (Vb).—The 50-ml aliquot of VI was added to a 25-ml ether solution containing an excess of diethylamine. After 30 min of stirring at room temperature the solution was filtered and the solvent was evaporated *in vacuo*. The resulting yellow oil was crystallized from hexane–methanol and yielded 0.50 g (28%) of white, crystalline Vb: mp 57–58°; nmr ($CDCl_3$) 0.79 (t, 6, methyl H), 2.51 (q, 4, methylene H), and 7.41 (m, 10, ArH); mass spectrum *m/e* 317 (parent ion) and 210 (base peak, p − Et_2NCl).

3,4-Dichloro-2,5-diphenylthiophene (IX).—A 10-ml solution of 1.92 g (0.01 mol) of diphenylbutadiyne and a 10-ml solution of 1.03 g (0.01 mol) of sulfur dichloride both in methylene chloride were simultaneously added over a 20-min period to 10 ml of stirred, ice-cooled methylene chloride. After stirring for an additional 2 hr at 0°, the solvent was removed from the dark solution *in vacuo*. After redissolving the dark, viscous mass in methylene chloride, it was percolated through a short column packed with neutral alumina (Woelm) in ether. Crystallization from acetone afforded 0.50 g (17%) of yellow, crystalline IX, mp 133–135°. Repeated recrystallization from acetone gave very faintly yellow crystals: mp 136–137° (lit.[20] mp 127–129°); mass spectrum *m/e* 306 (70% of 304, p + 2) and 304 (parent ion).

Anal. Calcd for $C_{16}H_{10}SCl_2$: C, 62.96; H, 3.30; S, 10.50; Cl, 23.23. Found: C, 62.93; H, 3.30; S, 10.54; Cl, 23.34.

2-Chloro-1-phenylethenesulfenyl Chloride (XII).—A solution containing 4.00 g (39.2 mmol) of phenylacetylene in 150 ml of dry methylene chloride was added over a 3-hr period to a rapidly stirred solution of 4.04 g (39.2 mmol) of sulfur dichloride in 350 ml of refluxing methylene chloride. Evaporation of the solvent left a red-orange, *foul*-smelling liquid. Analysis by nmr revealed complete loss of phenylacetylene.

Distillation gave 3.50 g (43%) of red-orange liquid collected at 74–78° (0.25 mm). It is important that the lowest possible pot temperature be maintained during this distillation to avoid excessive polymerization of the product. The mass spectrum showed no parent ion but had peaks at *m/e* 174 (65% of 172, therefore Cl_2 present), 172 (p − S), 139 (33% of 137, therefore one chlorine), 137 (p − SCl), and 105 (base peak); nmr (CCl_4) 6.79 (s, 1, olefinic H) and 7.37 (m, 5, ArH). Addition of phenylacetylene to a methylene chloride solution of XII gave XI as a

(20) C. L. Moyle and L. R. Drake, U. S. Patent 2,527,372 (1950). No other information concerning this compound is provided other than a chlorine analysis of 21.7%. We feel that their assignment of structure is at least questionable.

mixture of inseparable isomers as determined by nmr and mass spectroscopy.

Phenyl 2-Chloro-1-phenylethene Disulfide (XIII).—A solution of 0.268 g (2.44 mmol) of thiophenol in 5 ml of dry ether was added to a stirred solution of 0.50 g (2.44 mmol) of XII in 20 ml of dry ether at room temperature. After 15 min the ether was evaporated *in vacuo* to leave 0.68 g (100%) of viscous, rather unstable yellow liquid (XIII): nmr (CCl_4) 6.49 (s, 1, vinyl H) and 7.19 (m, 10, ArH). The mass spectrum showed no parent ion but proved the incorporation of thiophenol by the spectrum's base peak at 109 (PhS).

Addition of diethylamine to XII in the same fashion afforded the unstable N,N-diethylsulfenamide derivative (XIV): nmr (CCl_4) 1.06 (t, 6, methyl H), 2.80 (q, 4, methylene H), 6.30 (s, 1, olefinic H), and 7.31 (complex m, 5, ArH).

General Procedure for Competition Reactions.—A solution of 0.5 equiv of sulfur dichloride in 10 ml of dry ether was added over 15 min to a stirred solution containing 1 equiv each of alkene and alkyne in 20 ml of dry ether at 30° (molar ratio, SCl_2 to alkene to alkyne of 0.5:1:1). Stirring was continued for 0.5 hr and the solvents were evaporated. Products were immediately examined by nmr and areas were correlated to the relative amounts of the various products.

Registry No.—Sulfur dichloride, 10545-99-0; III, 23852-88-2; IV, 2326-63-8; Va, 23852-90-6; Vb, 23852-91-7; Vc, 23852-92-8; VIII, 23852-93-9; IX, 23852-94-0; XII, 23852-95-1.

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Stereoselectivity in the Debromination of the Stilbene Dibromides by Several Metals and Inorganic Reductants in Several Solvents[1a]

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If *meso*-stilbene dibromide is debrominated by any reductant in any solvent, the product is always 100% *trans*-stilbene. With *dl*-stilbene dibromide, the debromination results are variable: two-electron reductants such as iodide, platinum(II), benzenesulfinate, thiophenolate, and hydride yield *ca.* 75–90% *cis;* one-electron reductants, such as β-naphthol, copper(I), iron(II), chromium(II), titanium(III), etc., yield *ca.* 0–4% *cis;* metals such as zinc, cadmium, tin, etc., in a variety of solvents, yield variable quantities of *cis* (<25%). We have tentatively suggested a carbonium ion process (eq 4) for the two-electron reductants, a radical process for the one-electron reductants, and a surface radical process for the metals. Three factors appear to determine the stereochemical course of these redox reactions, namely, the electronic (orbital) and conformational preference for *anti* over *syn* elimination and the nature of the reductant (mechanism).

Normally, 1,2 dehalogenation in solution occurs in the *anti* sense[2,3] as is shown in the following equation.

$$\underset{\textit{meso}\text{ or }\textit{dl}}{(C_6H_5CHBr)_2} + M \longrightarrow \underset{\textit{trans}\text{ or }\textit{cis}}{C_6H_5CH{=}CHC_6H_5} + MBr_2 \quad (1)$$

There are enough interesting cases of *syn* dehalogenation, however, to make decisions about the mechanism(s) equivocal.[3-7] In this survey of reductants, we posed two questions: could we find conditions under which the debrominations of the stilbene dibromides were clearly *anti*, and equally could we find conditions under which these debrominations were wholly *syn*?

As a reaction type, dehalogenation goes back a long time; iodide-promoted elimination was used on coumarin dibromide by Perkin[8] and has since been used in series as simple as the 1,2-diiodoethylenes[3] or as complex as steroid dibromides.[9] Variants on the dihalide may include substitution of hydroxy, alkoxy, acetoxy, tosylate, etc., for one or both of the halogen atoms.[2,10] Among the many possible dehalogenating agents are sodium in tetrahydrofuran[11] or liquid ammonia,[12] iron(II),[13] vanadium(II),[14] titanium(III),[14] cadmium,[15] lithium,[16] phosphines,[17] phosphites,[18] thiolates,[19] selenide,[20] acetate,[17] carbonate,[17] hydroxide,[19] triethyltin hydride,[21] cobalt(II),[22] etc.[9b] (see also below and Tables I and II). It is useful to look at the overall process (eq 1) either as a nucleophilic attack on positive halogen or as a redox process involving a two-electron reduction of the dihalide (oxidant).[10]

meso-Stilbene dibromide has frequently been chosen as a model compound. However, the results of debromination are always the same: under a wide variety of conditions, *trans*-stilbene is the exclusive product. Some results have been tabulated;[9b] we shall indicate several reductants here: ethanol,[23] phenyl-

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