# Addition of Sulfonyl Chlorides to Acetylenes. II.[1] Stereoselective Control in the Syntheses of β-Chlorovinyl Sulfones

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The stereoselective, free-radical, copper-catalyzed addition of benzenesulfonyl chloride to phenylacetylene could be controlled by polar factors to give preferentially either trans or cis addition products. Excess chloride ions, or highly polar solvents, promoted formation of trans addition products, while cis addition predominated in low polarity solvents (*e.g.*, carbon disulfide). Acetonitrile had an exceptional behavior. The kinetically controlled trans addition product was isomerized with difficulty to the thermodynamically more stable stereoisomer. The photochemical isomerization of both isomers and suggested mechanisms for the addition reaction are discussed. Stereoselective addition of para-substituted benzenesulfonyl chlorides to phenylacetylene and characterization of these adducts are described.

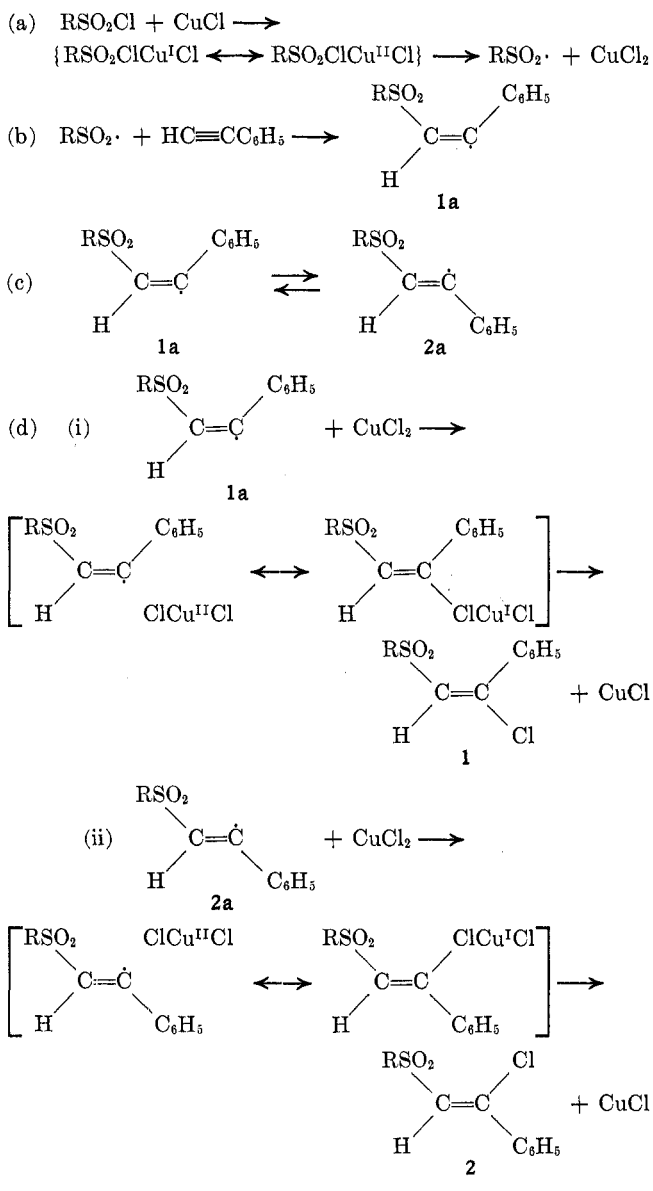
The stereoselective, copper-catalyzed addition of sulfonyl chlorides to phenylacetylene by a free-radical, redox-transfer chain mechanism was reported in the preceding paper. Since the addition was stereoselective, it was of interest to find conditions to alter the ratio of cis–trans adducts.

The overall reaction can be visualized by a frequently encountered mechanism for radical additions to acetylenes[2,3] assuming a trans addition.[4] This consists of four essential steps: (a) formation of sulfonyl radicals by cuprous chloride *via* a chlorine atom abstraction;[5] (b) attack by sulfonyl radicals on the terminal carbon of phenylacetylene with consequent formation of a resonance-stabilized cis intermediate radical (**1a**); (c) partial inversion of the trigonal carbon radical (**1a**) into a trans intermediate radical (**2a**) by equilibration to favor under specific reaction conditions, a more stable configuration; (d) in the product-forming step, scavenging of both isomeric radicals by cupric chloride, by a ligand-transfer process,[6] probably, in competition with each other due to polar and steric factors[7] (see Scheme I).

Several investigations dealing with the cis–trans isomerization of vinyl and styryl radicals have been reported[8] and values of the barrier of inversion for some of these radicals have been estimated.[3,7]

Considering the above stereoselectivity controlling factors, attempts were made to examine if the cis–trans distribution could be changed by varying experimental parameters. Also, it was desired to get more of the

SCHEME I




cis addition products which were obtained as minor by-products. There are no general synthetic routes to the corresponding *trans*-β-chlorovinyl sufides, which have been previously used as precoursers of these compounds. The only reported cis addition product, $p$-$CH_3C_6H_4SO_2CH{=}CClC_6H_5$, was obtained by oxidation of β-chlorovinyl sulfide, which was formed in minor

(1) Part I: Y. Amiel, *J. Org. Chem.*, **36**, 3691 (1971).

(2) R. A. Benkeser and R. A. Hickner, *J. Amer. Chem. Soc.*, **80**, 5298 (1958); R. A. Benkeser, M. L. Burrous, L. E. Nelson, and J. W. Swisher, *ibid.*, **83**, 4385 (1961); A. A. Oswald, K. Griesbaum, B. E. Hudson, Jr., and J. M. Bregman, *ibid.*, **86**, 2877 (1964); A. A. Oswald and K. Griesbaum in "The Chemistry of Organic Sulfur Compounds," Vol. 2, N. Kharasch and C. Y. Meyers, Ed., Pergamon Press, Elmsford, N. Y., 1966, p 233; K. Griesbaum, *Angew. Chem., Int. Ed. Engl.*, **9**, 273 (1970).

(3) P. S. Skell and R. G. Allen, *J. Amer. Chem. Soc.*, **86**, 1559 (1964).

(4) W. E. Truce and J. A. Simms, *ibid.*, **78**, 2756 (1956); S. I. Miller, *ibid.*, **78**, 6091 (1956).

(5) A. Orochov, M. Asscher, and D. Vofsi, *J. Chem. Soc. B*, 255 (1969); M. Asscher and D. Vofsi, *ibid.*, 947 (1968), and preceding papers.

(6) D. C. Nonhebel and W. A. Waters, *Proc. Roy. Soc., Ser. A*, **242**, 16 (1957); C. H. Bamford, A. D. Jenkins, and R. Johnston, *Trans. Faraday Soc.*, **55**, 418 (1959); F. Minisci and R. Galli, *Tetrahedron Lett.*, 533 (1962); J. K. Kochi, *Tetrahedron*, **18**, 483 (1962); *J. Amer. Chem. Soc.*, **84**, 2785 (1962); *Science*, **155**, 415 (1967).

(7) L. A. Singer and N. P. Kong, *J. Amer. Chem. Soc.*, **88**, 5213 (1966); *Tetrahedron Lett.*, 2089 (1966); *ibid.*, 4849 (1969); R. M. Kopchik and J. A. Kampmeier, *J. Amer. Chem. Soc.*, **90**, 6733 (1968).

(8) G. D. Sargent and M. W. Browne, *ibid.*, **89**, 2788 (1967); W. G. Bentrude, *Annu. Rev. Phys. Chem.*, **18**, 300 (1967); O. Simamura, *Top. Stereochem.*, **4**, 21 (1969); M. Julia in "Chemistry of Acetylenes," H. G. Viehe, Ed., Marcel Dekker, New York, N. Y., 1969, p 345; L. A. Singer, *Intra-Sci. Chem. Rep.*, **4**, 139 (1970).

TABLE I

REACTIONS OF SULFONYL CHLORIDES (10 MMOL) WITH PHENYLACETYLENE (11 MMOL) IN THE PRESENCE OF CUPRIC CHLORIDE (0.2 MMOL) AND CHLORIDE SALT[a] (0.3 MMOL) IN ACETONITRILE (3 G) AT 100°

| No. | $RSO_2Cl$ | Chloride | Time, hr | Conversion,[b] % | Adduct distribution, %: 1 (R = $C_6H_5$) | 2 (R = $C_6H_5$) |
|---|---|---|---|---|---|---|
| 1 | $C_6H_5$ | $NEt_3HCl$ | 4 | 84 | 92 | 8 |
| 2 | $C_6H_5$ | LiCl | 4 | 78 | 90 | 10 |
| 3 | $C_6H_5$ | | 6 | 85 | 17 | 83 |
| 4 | $CH_3$ | $NEt_3HCl$ | 16 | 73 | 96 | 4 |
| 5 | $CH_3$ | | 16 | 75 | 7 | 93 |

[a] If indicated. [b] Calculated on sulfonyl chloride consumed.

Essentially the same effect was obtained when lithium chloride was used instead of the ammonium chloride.

A dramatic change was noted when experiments were conducted with copper(I or II) chloride catalyst in the absence of triethylammonium (or lithium) chloride; almost a complete reversal of cis–trans distributions was obtained (see Table I).

**Solvent Effects.**—It was found that solvent polarity also had a remarkable influence on the adduct distribution. Surprisingly, trans addition product (**1**, R = $C_6H_5$) was predominantly obtained, even in the absence of added chlorides, when the reactions were run in solvents with a high dielectric constant; the cis addition product (**2**, R = $C_6H_5$) was predominantly formed in solvents with a low dielectric constant. A striking reversal was again observed when a chloride salt was added to solvents of the latter kind, *e.g.*, carbon disulfide (see Table II, no. 9 and 10).

TABLE II

REACTIONS OF BENZENESULFONYL CHLORIDE (10 MMOL) WITH PHENYLACETYLENE (11 MMOL) IN THE PRESENCE OF COPPER CATALYST AND TRIETHYLAMMONIUM CHLORIDE[a] (1, 5 MMOL) IN VARIOUS SOLVENTS AT 100°

| No. | $CuCl_2$, mmol | Solvent (g) | Additive (g) | Time, hr | Conversion, %[b] | Adduct distribution, %: 1 (R = $C_6H_5$) | 2 (R = $C_6H_5$) |
|---|---|---|---|---|---|---|---|
| 1 | 0.25 | Nitrobenzene (4) | | 12 | 69 | 94 | 6 |
| 2 | 0.25 | Nitrobenzene (1) | Acetonitrile (1) | 5 | 59 | 36 | 64 |
| 3 | 0.25 | *N*-Hexamethylphosphoric triamide (1) | | 12 | 61 | 95 | 5 |
| 4 | 0.25 | *N*-Hexamethylphosphoric triamide (1) | Acetonitrile (1) | 5 | 63 | 44 | 56 |
| 5 | 0.25 | Tetramethylene sulfone (1) | | 5 | 66 | 93 | 7 |
| 6 | 0.25 | Tetramethylene sulfone (1) | Acetonitrile (1) | 5 | 70 | 26 | 74 |
| 7 | 0.25 | Pyridine (3) | | 5 | 34 | 88 | 12 |
| 8 | 0.5 | Diglyme (3) | | 4 | 75 | 16 | 84 |
| 9 | 0.5 | Carbon disulfide (5) | | 16 | 81 | 16 | 84 |
| 10 | 0.5 | Carbon disulfide (5) | $NEt_3HCl$ (1.5 mmol) | 16 | 88 | 82 | 18 |

[a] If indicated. [b] Calculated on sulfonyl chloride consumed.

quantities as a by-product.[9] These adducts are also interesting because, unlike the trans addition products, they easily undergo β-trans-dehydrochlorination to give the corresponding α-ethynyl sulfones.[1]

## Results

The following experiments describe modifications which turned out to be of major importance in controlling the stereochemical course of this addition reaction. To favor formation of cis addition isomers (**2**), an attempt was made to reduce the efficiency of step d, thus altering competition with step c.

**Effect of Added Chloride Ions.**—As described previously,[1] triethylammonium chloride was used in addition to the cupric chloride catalyst. By adding chloride ions, chlorocuprates are formed; these complexes are more soluble in acetonitrile and are known to be very efficient radical scavengers,[10] thus making step d faster.

**Acetonitrile as Solvent.**—Acetonitrile exhibited an unusual behavior, different from the other dipolar, aprotic solvents (see Table II, no. 1, 3, and 5); unexpectedly, **2** was predominantly formed (see Table I, no. 3). The distribution was shifted in favor of cis addition product when acetonitrile was added in a 1:1 ratio to other dipolar, aprotic solvents (see Table II, no. 1–6). The extent of formation appeared to be dependent on the amount of acetonitrile (see Table III, no. 2 and 3).

**Cuprous Chloride, Instead of Cupric Chloride, as the Catalyst.**—Table III shows that cuprous chloride behaves essentially like cupric chloride, perhaps favoring somewhat the formation of **2**. The same result was obtained with equimolar amounts of cuprous chloride and sulfonyl chloride in the presence of copper metal (see Table III, no. 4), in order to keep the concentration of cupric chloride as low as possible, thus expecting a decrease in rate of step d. It is clear, though, that no special effect is observed.

**Stereoselective Syntheses of Para-Substituted Benzenesulfonyl Chlorides to Phenylacetylene.**—Stereoselective syntheses of the following cis and trans addi-

(9) V. Caló, G. Modena, and G. Scorrano, *J. Chem. Soc. C*, 1339, 1344 (1968). The addition of sulfenyl chlorides to a triple bond [F. Montanari, *Gazzetta*, **86**, 735 (1956); W. E. Truce and M. M. Boudakian, *J. Amer. Chem. Soc.*, **78**, 2748 (1956); L. Benati, M. Tiecco, and A. Tundo, *Boll. Sci. Fac. Chim. Ind. Bologna*, **21**, 177 (1963); A. Dondoni, G. Modena, and G. Scorrano, *ibid.*, **22**, 26 (1964)], as well as to a double bond [D. J. Cram, *J. Amer. Chem. Soc.*, **71**, 3883 (1949); A. J. Havlik and N. Kharasch, *ibid.*, **78**, 1207 (1956); G. H. Schmid and V. M. Csizmadia, *Can. J. Chem.*, **44**, 1338 (1966)] is known to occur in trans fashion.

(10) J. K. Kochi and D. M. Mog, *J. Amer. Chem. Soc.*, **87**, 522 (1965).

TABLE III

REACTIONS OF BENZENESULFONYL CHLORIDE (10 MMOL) WITH PHENYLACETYLENE (11 MMOL) IN THE PRESENCE OF COPPER CHLORIDE CATALYST AND TRIETHYLAMMONIUM CHLORIDE[a] IN ACETONITRILE, 6 HR AT 100°

| No. | Copper catalyst (mmol) | $NEt_3HCl$, mmol | Acetonitrile, g | Conversion, %[b] | Adduct distribution, % 1 (R = $C_6H_5$) | 2 (R = $C_6H_5$) |
|---|---|---|---|---|---|---|
| 1 | CuCl (0.6) | 1.8 | 3 | 78 | 94 | 6 |
| 2 | CuCl (0.6) | | 1 | 82 | 12 | 88 |
| 3 | CuCl (0.6) | | 7 | 87 | 44 | 56 |
| 4 | CuCl (10) Cu powder (0.04[c]) | | 7 | 92 | 43 | 57 |
| 5 | CuCl (0.01) | | 2 | 18[d] | 20 | 80 |
| 6 | CuCN (0.2) | | 3 | 71 | 24 | 76 |
| 7 | CuCN (0.01) | | 2 | 12[d] | 22 | 78 |
| 8 | $Cu(OAc)_2 \cdot H_2O$ (0.1) | | 2 | 14 | 85 | 15 |

[a] If indicated. [b] Calculated on sulfonyl chloride consumed. [c] Gram-atoms. [d] In these experiments small amounts (*ca.* 50 mg) of 1,3,5-triphenylbenzene, mp 170°, were isolated.

TABLE IV

REACTIONS OF *p*-TOLUENESULFONYL CHLORIDE (20 MMOL) WITH PHENYLACETYLENE (21 MMOL) IN THE PRESENCE OF A COPPER CATALYST AND TRIETHYLAMMONIUM CHLORIDE[a] AT 100° IN THE FOLLOWING SOLVENTS

| No. | Copper catalyst (mmol) | $NEt_3HCl$, mmol | Solvent (g) | Time, hr | Conversion, %[b] | Adduct distribution, % 3 (R = $CH_3$) | 4 (R = $CH_3$) |
|---|---|---|---|---|---|---|---|
| 1 | $CuCl_2$ (0.2) | 0.4 | Acetonitrile (7) | 16 | 88 | 92 | 8 |
| 2 | $CuCl_2$ (0.2) | | Tetramethylene sulfone (2) | 16 | 74 | 94 | 6 |
| 3 | $CuCl_2$ (0.2) | | Acetonitrile (7) | 8 | 80 | 48 | 52 |
| 4 | CuCl (0.2) | | Acetonitrile (1) | 12 | 72 | 25 | 75 |
| 5 | CuCl (0.2) | | Acetonitrile (3) | 12 | 78 | 29 | 71 |
| 6 | CuCl (0.2) | | Acetonitrile (7) | 12 | 85 | 35 | 65 |
| 7 | CuCN (0.1) | | Acetonitrile (2) | 8 | 75[c] | 30 | 70 |
| 8 | CuCl (0.1) | | Diglyme (5) | 12 | 70 | 38 | 62 |
| 9 | CuCl (0.3) | | Carbon disulfide (5) | 16 | 74 | 26 | 74 |

[a] If indicated. [b] Calculated on sulfonyl chloride consumed. [c] See footnote *d*, Table III.

TABLE V

REACTIONS OF *p*-CHLOROBENZENESULFONYL CHLORIDE (20 MMOL) WITH PHENYLACETYLENE (21 MMOL) IN THE PRESENCE OF COPPER(I OR II) CHLORIDE AND TRIETHYLAMMONIUM CHLORIDE[a] AT 100° IN THE FOLLOWING SOLVENTS

| No. | Copper chloride (mmol) | $NEt_3HCl$ mmol | Solvent (g) | Time, hr | Conversion, %[b] | Adduct distribution, % 3 (R = Cl) | 4 (R = Cl) |
|---|---|---|---|---|---|---|---|
| 1 | $CuCl_2$ (0.2) | 0.4 | Acetonitrile (3) | 3 | 96 | 93 | 7 |
| 2 | $CuCl_2$ (0.2) | | Acetonitrile (3) | 3 | 90 | 34 | 66 |
| 3 | CuCl (0.2) | | Acetonitrile (3) | 3 | 92 | 31 | 69 |
| 4 | CuCl (0.2) | | Carbon disulfide (5) | 6 | 88 | 27 | 73 |

[a] If indicated. [b] Calculated on sulfonyl chloride consumed.

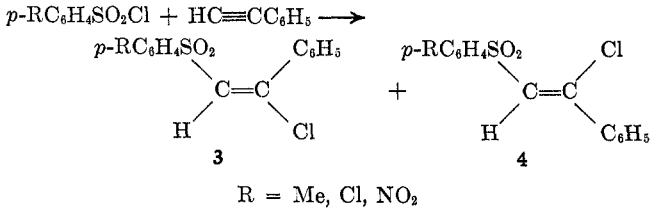
TABLE VI

REACTIONS OF *p*-NITROBENZENESULFONYL CHLORIDE (20 MMOL) WITH PHENYLACETYLENE (21 MMOL), IN THE PRESENCE OF COPPER(I OR II) CHLORIDE AND TRIETHYLAMMONIUM CHLORIDE[a] AT 100° IN THE FOLLOWING SOLVENTS

| No. | Copper chloride (mmol) | $NEt_3HCl$, mmol | Solvent (g) | Time, hr | Conversion, %[b] | Adduct distribution, % 3 (R = $NO_2$) | 4 (R = $NO_2$) |
|---|---|---|---|---|---|---|---|
| 1 | $CuCl_2$ (0.2) | 0.4 | Acetonitrile (2) | 3.5 | 94 | 93 | 7 |
| 2 | $CuCl_2$ (0.2) | | Acetonitrile (10) | 4.5 | 82 | 72 | 28 |
| 3 | $CuCl_2$ (0.2) | | Acetonitr le (2) | 4.5 | 88 | 46 | 54 |
| 4 | CuCl (0.2) | | Acetonitrile (2) | 4.5 | 92 | 42 | 58 |
| 5 | CuCl (0.2) | | Carbon disulfide (5) | 12 | 72 | 45 | 55 |

[a] If indicated. [b] Calculated on sulfonyl chloride consumed.

tion products under various conditions are shown in Tables IV–VI.




R = Me, Cl, $NO_2$

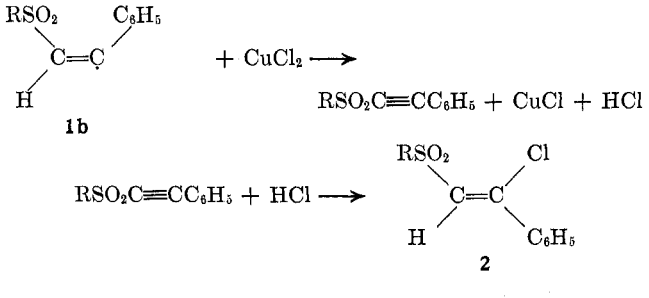
## Discussion

These experiments indicate that the addition reactions are strongly dependent on the polarity of the medium. Polar factors may have a pronounced role in homolytic reactions, particularly when polarizable species are involved. This appears to be so when highly electrophilic sulfonyl radicals attack a polar substrate and, moreover, when adduct formation takes place by a reduction–oxidation process involving copper-co-

ordination compounds. Solvation and coordination of participants may operate on the transition states, thus directing the course of adduct formation by stereoelectronic factors. Complex formation between sulfonyl radicals and solvent molecules with a $\pi$-electron system of an alkene has been reported.[11] Complex formation with nucleophilic solvents was shown to make radicals more selective; the reactivity of radicals toward abstractions is known to be considerably modified by the solvent.[12] The fact that trans addition product (1) is predominantly formed in high dielectric constant solvents could be attributed to the preferred solvent interactions with the less hindered radical[7] **1a**. Hence, a shift in the fast, configurational equilibration of the trigonal radicals (step c) in favor of **1a** would lead to the formation of the kinetically controlled trans addition product (1). Redox potentials and bond dissociation energies, which affect step d, are also solvent dependent. It would be difficult to differentiate between the solvent effects on the equilibration process (step c), or on the transition states in step d, which affects the bond dissociation required for the chlorine transfer.

The exceptional behavior of acetonitrile is presently unclear, but this may reflect weaker complexing power toward the compound radical **1a**, compared with the other aprotic, dipolar solvents, enabling more equilibration (step c) to take place. It might be also that in this solvent the product-forming, ligand transfer, step d is less efficient. It is known that Cu(II) and chloride ions are weakly solvated in acetonitrile[13] and cuprous species are more stabilized in this solvent.[14] Cuprous species are stronger chloride ion acceptors than Cu(II) ions; consequently, retardation in chlorine-atom transfer would be anticipated. However, when additional chloride ions are added, a mass-action effect shifts the equilibria and higher chlorocupric complexes are formed and, indeed, the complexes were shown to be very efficient radical scavengers.[10,15]

Although the proposed mechanism for the formation of cis addition product *via* a trans addition process followed by isomerization of the intermediate radical is plausible, more experimental evidence would be desired. There exists also the possibility of a concurrent cis addition as a result of a concerted reaction mechanism. Another route leading to cis addition products could be described by the following elimination–addition process.




**1b** **2**

In this oxidative elimination, electron-transfer step,[6] $\alpha$-ethynyl sulfone is presumably formed; in the subsequent step trans addition of HCl would take place. Such an elimination–addition process would be particularly inconceivable in the case of a nonterminal acetylene, such as diphenylacetylene.[1]

Several experiments were carried out to attempt the isomerization of the kinetically formed trans addition product, *via* addition–elimination of sulfonyl radicals, into the thermodynamically more stable planar adduct. The trans addition product (**1**, R = $C_6H_5$) was heated with a sulfonyl chloride, in the presence of copper chloride, under conditions which favored formation of **2** (R = $C_6H_5$). After 22 hr at 100°, only 10% of the adduct was converted into the corresponding isomer (**2**, R = $C_6H_5$), whereas the rest was recovered unchanged. The cis addition product (**2**) did not isomerize under these conditions, and in both cases no diaddition product was found. This strongly suggests that sulfonyl radicals, which are generated in the same way as in the original addition reaction, are very inefficient in attacking the double bond; this is probably due to either steric reasons or because of the strong inductive effect of the electron-withdrawing sulfonyl group, which diminishes the reactivity of the olefinic bond toward radicals of an electrophilic nature.

The photochemical isomerization of 2-benzenesulfonyl-1-chlorostyrenes worked very well, because both the cis (**1**, R = $C_6H_5$) and the trans (**2**, R = $C_6H_5$) isomers gave the same photostationary state cis (85%)–trans (15%) mixture.

The reactivity of para-substituted benzenesulfonyl chlorides was, as expected, shown to be dependent on the inductive effects of the para substituents. Generation of sulfonyl radicals was much faster with electron-withdrawing substituents,[16] while *p*-toluenesulfonyl chloride was much less reactive, due to the opposite inductive effect of the methyl group. The copper-catalyzed, redox-transfer, chain additions of substituted aromatic sulfonyl chlorides, as demonstrated in the case of styrene,[5] were shown to follow Hammett's rule; the observed small substituent effects also indicated that atom transfers rather than electron transfers operate in such reactions.

Structural proof and configurational assignment were based on the same criteria as previously described.[1] The known trans addition products (**3**, R = $CH_3$, $NO_2$)[9] were obtained previously by oxidation of the corresponding $\beta$-chlorovinyl sulfides.

Reductions of the cis and trans addition products gave, in each case, the same saturated sulfone. The configuration of the stereoisomers was based on spectral evidence, as discussed earlier.[1] Products having the trans addition structure have ultraviolet absorptions at shorter wavelengths; the isomeric adducts showed bathochromic shifts of the styryl band and had much stronger intensities (see Table VII). Infrared spectra proved to be valuable, particularly in identifying chromatography as shown previously.[1]

In the nmr spectra, the vinylic protons were shown to be more deshielded in the coplanar configurations (**4**) than in the corresponding noncoplanar adducts (**3**) as mentioned earlier.[1] Additional splitting of four

(11) E. S. Huyser and L. Kim, *J. Org. Chem.*, **32**, 618 (1967).
(12) G. A. Russell, *J. Amer. Chem. Soc.*, **80**, 4987 (1958); C. Walling and M. F. Mayahi, *ibid.*, **81**, 1485 (1959).
(13) I. V. Nelson, R. C. Larson, and R. T. Iwamoto, *J. Inorg. Nucl. Chem.*, **22**, 279 (1961).
(14) R. C. Larson and R. T. Iwamoto, *J. Amer. Chem. Soc.*, **82**, 3239 (1960).
(15) M. Talât-Erben and N. Önal, *Can. J. Chem.*, **38**, 1154 (1960).
(16) E. C. Ladd, U. S. Patent 2,573,580 (1952); *Chem. Abstr.*, **46**, 7588 (1952).

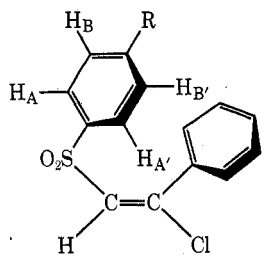
TABLE VII

ULTRAVIOLET SPECTRA

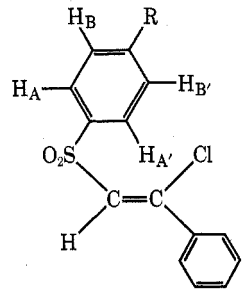
| | 3 | | | | 4 | | | |
|---|---|---|---|---|---|---|---|---|
| | Phenyl bands | | Styryl bands | | Phenyl bands | | Styryl bands | |
| R | $\lambda_{max}$ | $\epsilon$ | $\lambda_{max}$ | $\epsilon$ | $\lambda_{max}$ | $\epsilon$ | $\lambda_{max}$ | $\epsilon$ |
| H | 212 | 16,000 | 262 | 10,000 | 212, 219 | 15,500 | 275 | 20,000 |
| $CH_3$ | 209 | 18,500 | 246 | 12,500 | 212, 219 | 14,000 | 276 | 20,000 |
| Cl | 213 | 15,000 | 241 | 14,500 | 212, 219 | 15,500 | 276 | 20,500 |
| $NO_2$ | 213 | 18,000 | 256 | 15,500 | 212 | 17,000 | 286 | 20,000 |

TABLE VIII

NMR DATA[a] OF *p*-BENZENESULFONYL ADDITION PRODUCTS




3




4

| | 3 | | | | | 4 | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Phenyl protons | | | | | Phenyl protons | | |
| R | Vinyl protons (s) | Methyl protons (s) | AA′ (d) | BB′ (d) | Remaining (m) | Vinyl protons (s) | Methyl protons (s) | AA′ (d) | BB′ (d) | Remaining (m) |
| $CH_3$ | 6.93[9] | 2.35 (3 H) | 7.51 | 7.15 | 7.36 (5 H) | 7.16 | 2.45 (3 H) | 7.97 | 7.36 | 7.26–7.75 (5 H) |
| | | | $J$ = 8.5 | | | | | $J$ = 8.5 | | |
| Cl | 6.93 | | 7.40[b] | | 7.26–7.36 (7 H) | 7.17 | | 8.00 | 7.44 | 7.20–7.36 (5 H) |
| | | | $J$ = 4 | | | | | $J$ = 8.5 | | |
| $NO_2$ | 7.02 | | 7.77 | 8.23 | 7.25–7.59 (5 H) | 7.22 | | 8.27 | 8.50 | 7.45–7.79 (5 H) |
| | | | $J$ = 9 | | | | | $J$ = 9 | | |

[a] Measured in $CDCl_3$ on a Varian A-60 with TMS as internal standard; chemical shifts reported in $\delta$ (ppm) and apparent spin couplings ($J$) in Hz units; s = singlet, d = doublet, m = multiplet. [b] Partial overlap.

deshielded protons of the para-substituted benzene ring were also quite characteristic. These four protons appeared as a typical AA′BB′ pattern for a para-disubstituted phenyl ring. Spectral comparisons (see Table VIII) indicated that the protons ortho to the electronegative sulfone group ($H_A$ and $H_{A'}$) were more deshielded than those in the meta positions ($H_B$ and $H_{B'}$) in *p*-methyl- (**3** and **4**, R = $CH_3$) and in *p*-chlorobenzenesulfonyl adducts (**3** and **4**, R = Cl); however, a reversed order is suggested for the *p*-nitro adducts (**3** and **4**, R = $NO_2$), in which the deshielding effect of the nitro group is much stronger than that of the sulfone group. These protons were more shielded in the trans addition products than in the cis addition isomers (see Table VIII), due to the proximity in space of the two phenyl rings (see **3**).[1] A similar, small shielding effect of the phenyl ring on the protons of the *p*-methyl group was noted in **3** (R = $CH_3$) as compared to **4** (R = $CH_3$) (see Table VIII).

## Experimental Section[17]

**Materials.**—Phenylacetylene and methanesulfonyl and benzenesulfonyl chlorides, from Fluka (puriss), were distilled before use; para-substituted benzenesulfonyl chlorides (Eastman Kodak, White Label) were dissolved in methylene chloride, washed with ice–water, dried ($CaCl_2$), and after evaporation of solvent recrystallized from 2-propanol; *p*-toluenesulfonyl chloride and *p*-chlorobenzenesulfonyl chloride were distilled before recrystallization; anhydrous cupric chloride was obtained from the dihydrate (B. D. H., reagent grade) by dehydration at 110° to constant weight; triethylammonium chloride (B. D. H., reagent grade) was crystallized from 2-propanol and dried at 100°; acetonitrile (Fluka, puriss) was distilled over $P_2O_5$; nitrobenzene (puriss), *N*-hexamethylphosphoric triamide (pract), tetramethylene sulfone (purum), and pyridine (purum) were refluxed over KOH pellets and then distilled; diglyme (pract), carbon disulfide (purum), cuprous chloride (purum), lithium chloride (purum), and benzophenone (purum) were obtained from Fluka; and Florisil (100–200 mesh) was obtained from Floridin Co.

**(*E,Z*)-2-Benzenesulfonyl(or 2-Methanesulfonyl)-1-chlorostyrenes (1 and 2, R = $C_6H_5$, $CH_3$).**—These addition reactions were carried out in Carius tubes which were sealed at 0.1 mm after degassing (three times) according to the amounts and conditions described in Tables I–III. Rates of reactions were followed by dilatometry. After contraction stopped, the tube was cooled in ice–water and opened. The reaction mixtures were usually dissolved in methylene chloride and transferred to a separatory funnel, washed with water and with an aqueous solution of disodium ethylenediaminetetraacetate until free from copper; the organic layer was dried ($Na_2SO_4$) and the crude material, which was obtained after evaporation of the solvent, was subjected to column chromatography, using Florisil. Elutions with *n*-hexane afforded unreacted sulfonyl chloride and phenylacetylene (if indicated), and small amounts (*ca.* 50 mg) of 1,3,5-triphenylbenzene, mp 170° (see Table III, no. 5 and 7), which had the correct analysis and was compared with an authentic sample. Elutions with ether–*n*-hexane (1:3) gave the trans addition products (**1**, R = $C_6H_5$, $CH_3$), while cis addition isomers (**2**, R = $C_6H_5$, $CH_3$) were eluted with ether–*n*-hexane (1:1). The characterization of these adducts was described in the preceding paper.

**(*E,Z*)-2-(Para-substituted benzenesulfonyl)-1-chlorostyrenes (3 and 4).**—These addition reactions were carried out in Carius tubes which were sealed at 0.1 mm after degassing (three times) according to the amounts and conditions described in Tables IV–VI. Rates of reactions were followed by dilatometry. After contraction stopped, the tube was cooled in ice–water and opened. The reaction mixtures were usually dissolved in methy-

(17) All melting points are uncorrected. Ir spectra were determined on a Perkin-Elmer Model 125 or 237B spectrophotometer; uv spectra were obtained in aqueous $C_2H_5OH$ on a Cary Model 14M spectrophotometer. Irradiation was conducted using Hanau Q81 high-pressure mercury vapor lamps. Microanalyses were performed in our microanalytical section directed by Mr. R. Heller.

lene chloride and transferred to a separatory funnel, washed with water and with an aqueous solution of disodium ethylenediaminetetraacetate until free from copper; the organic layer was dried ($Na_2SO_4$) and the crude material, which was obtained after evaporation of the solvent, was subjected to column chromatography, using Florisil. The first elutions, with ether–*n*-hexane (1:9), afforded some unreacted sulfonyl chloride and phenylacetylene (if indicated); trans addition products were eluted with ether–*n*-hexane (1:4), and the isomeric adducts with ether–*n*-hexane (1:1).

**(*E,Z*)-2-*p*-Toluenesulfonyl-1-chlorostyrenes (3 and 4, R = $CH_3$).**—These adducts were obtained using the above-described general procedure, and conditions given in Table IV. An induction period of 35 min was observed. 1,3,5-Triphenylbenzene (28 mg) was isolated from the earlier chromatographic fractions of experiment no. 7 (see Table IV). Recrystallizations from ethanol gave colorless needles of trans addition product (**3**, R = $CH_3$): mp 102.5–103.5° (lit.[9] mp 102–103°); ir ($CHCl_3$) 6.19, 6.22, 6.27, 6.92, 7.12, 7.22, 7.58, 7.65, 7.72, 8.1–8.2, 8.75, 9.25, 9.8, 10.76, 11.05, and 12.2 $\mu$.

*Anal.* Calcd for $C_{15}H_{13}ClO_2S$: C, 61.71; H, 4.48; Cl, 12.11; S, 10.95. Found: C, 61.48; H, 4.41; Cl, 12.07; S, 10.98.

Recrystallizations from methanol gave colorless prisms of cis addition product (**4**, R = $CH_3$): mp 124.5–125.5° (lit.[9] mp 123–124°); ir ($CHCl_3$) 6.28, 6.30, 6.36, 6.72, 6.92, 7.12, 7.22, 7.58, 7.65, 7.65, 7.77, 8.15–8.25, 8.75, 9.27, 9.8, 9.22, 9.98, 10.72, 10.92, and 12.2 $\mu$.

*Anal.* Calcd for $C_{15}H_{13}ClO_2S$: C, 61.71; H, 4.48; Cl, 12.11; S, 10.95. Found: C, 61.67; H, 4.46; Cl, 12.17; S, 11.05.

**Catalytic Reductions of 3 and 4 (R = $CH_3$).**—Reductions of 2-(*p*-toluenesulfonyl)-1-chlorostyrenes with $H_2$ over 5% Pd/C, in methanol at 25° and atmospheric pressure, gave in each case 2-phenylethyl *p*-tolyl sulfone.[18]

**(*E,Z*)-2-(*p*-Chlorobenzenesulfonyl)-1-chlorostyrenes (3 and 4, R = Cl).**—These adducts were obtained using the above-described general procedure, and conditions given in Table V. Recrystallizations from methanol gave colorless needles of trans addition product (**3**, R = Cl): mp 114.5–115.5°; ir ($CHCl_3$) 6.19, 6.27, 6.73, 6.92, 7.17, 7.58, 7.72, 7.82, 8.6, 8.68, 8.75, 9.77, 9.87, 10.75, 11.05, and 12.3 $\mu$.

*Anal.* Calcd for $C_{14}H_{10}Cl_2O_2S$: C, 53.68; H, 3.22; Cl, 22.64; S, 10.24. Found: C, 53.13; H, 3.40; Cl, 23.05; S, 10.95.

Recrystallizations from acetone–2-propanol gave colorless plates of cis addition product (**4**, R = Cl): mp 111.5–112.5°; ir ($CHCl_3$) 6.26, 6.36, 6.72, 6.92, 7.17, 7.58, 7.72, 7.83, 8.2, 8.75, 9.17, 9.22, 9.87, 10.72, 10.92, and 12.3 $\mu$.

*Anal.* Calcd for $C_{14}H_{10}Cl_2O_2S$: C, 53.68; H, 3.22; Cl, 22.64; S, 10.24. Found: C, 53.88; H, 3.19; Cl, 22.89; S, 10.41.

**(*E,Z*)-2-(*p*-Nitrobenzenesulfonyl)-1-chlorostyrenes (3 and 4, R = $NO_2$).**—These adducts were obtained using the above-described general procedure, and conditions given in Table VI. Recrystallizations from methanol gave colorless plates of trans addition product (**3**, R = $NO_2$): mp 127–128° (lit.[9] mp 123–125°); a transition point at 114° was noted, at which the compound melted and immediately solidified until the final melting point; ir ($CHCl_3$) 6.19, 6.27, 6.36, 6.53, 6.78, 6.92, 7.12, 7.25, 7.38, 7.58, 7.72, 7.8, 8.6, 8.73, 9.27, 9.8, 10.75, 10.05, 11.65, and 12.3 $\mu$.

*Anal.* Calcd for $C_{14}H_{10}ClNO_4S$: C, 51.95; H, 3.11; Cl, 10.95; N, 4.33; S, 9.91. Found: C, 51.92; H, 3.02; Cl, 11.03; N, 4.24; S, 10.02.

Recrystallization from methanol–ethyl acetate gave colorless plates of cis addition product (**4**, R = $NO_2$): mp 157–158°; ir ($CHCl_3$) 6.36, 6.4, 6.55, 6.72, 6.92, 7.12, 7.38, 7.52, 7.60, 8.08, 8.20, 8.74, 8.92, 9.22, 9.85, 10.73, 10.85, 11.6, and 12.3 $\mu$.

*Anal.* Calcd for $C_{14}H_{10}ClNO_4S$: C, 51.95; H, 3.11; Cl, 10.95; N, 4.33; S, 9.91. Found: C, 52.06; H, 2.97; Cl, 10.87; N, 4.27; S, 10.05.

**Isomerization of 1 (R = $C_6H_5$) into 2 (R = $C_6H_5$).**—A mixture of 139 mg (0.5 mmol) of adduct 1 (R = $C_6H_5$), 88 mg (0.5 mmol) of benzenesulfonyl chloride, and 6.9 mg (0.05 mmol) of cupric chloride in 0.25 g of acetonitrile was heated at 100° for 22 hr. The solvent and the unreacted benzenesulfonyl chloride were distilled off. The remaining solid residue, including catalyst, was chromatographed over 25 g of Florisil. Elution with ether–*n*-hexane (1:3) gave 120 mg of unchanged adduct 1 (R = $C_6H_5$) and further elution with ether–*n*-hexane (1:1) gave 14 mg (10% conversion) of the cis addition isomer (**2**, R = $C_6H_5$).

**Photochemical Isomerization.**—A solution of 1.39 g (5 mmol) either of trans addition product (1, R = $C_6H_5$) or cis addition isomer (**2**, R = $C_6H_5$) in 100 ml of benzene, in the presence of 1.5 g of benzophenone, as a photosensitizer, was irradiated for 2 hr by a Hanau Q81 high-pressure mercury vapor lamp fitted into Pyrex tubes. The lamp was immersed in the reaction mixture, which was cooled externally with running water, and oxygen-free nitrogen was passed through the mixture throughout the irradiation. The internal temperature was kept at 30–32°. The same photostationary mixture of the two addition products, 1 (R = $C_6H_5$) (85%) and **2** (R = $C_6H_5$) (15%) was isolated, after removal of solvent and benzophenone by high vacuum distillation, following adduct separation by column chromatography as previously reported. The adducts were identified by melting point and ir spectra as earlier described.

**Registry No.**—**3** (R = H), 31598-92-2; **3** (R = $CH_3$), 19738-00-2; **3** (R = Cl), 31599-05-0; **3** (R = $NO_2$), 31599-06-1; **4** (R = H), 31598-93-3; **4** (R = $CH_3$), 19738-01-3; **4** (R = Cl), 31599-09-4; **4** (R = $NO_2$), 31599-10-7; methanesulfonyl chloride, 124-63-0; benzenesulfonyl chloride, 98-09-9; *p*-toluenesulfonyl chloride, 98-59-9; *p*-chlorobenzenesulfonyl chloride, 98-60-2; *p*-nitrobenzenesulfonyl chloride, 98-74-8; phenylacetylene, 536-74-3; cupric chloride, 7447-39-4; cuprous chloride, 7758-89-6; triethylammonium chloride, 554-68-7; 1,3,5-triphenylbenzene, 612-71-5.

(18) E. P. Kohler and H. Potter, *J. Amer. Chem. Soc.*, **57**, 1316 (1935).