Anal. Calcd for $C_{18}H_{20}N_2O_2S_3$: C, 55.07; H, 5.14; N, 7.14; S, 24.50. Found: C, 54.64; H, 5.12; N, 6.87; S, 24.18.

Elution of the middle band and crystallization from ether gave 1.575 g (47%) of *N*-(2-cyanophenyl)-*N*-methylthiomethyl-*p*-toluenesulfonamide (**19a**): mp 97–98°; λ_{max}^{MeOH} 220 mμ (sh, ε 21,600), 276 (sh, 1700); ν_{max} (KBr) 2250, 1600, 1495 cm^{-1}; nmr ($CDCl_3$) 2.22 (s, 3, SMe), 2.37 (s, 3, ArMe), 4.70 (s, 2, NCH_2S), 7.4 ppm (m, 8, Ar); mass spectrum (70 eV) *m/e* 332 (M^+), 285 (M − SMe), 177 (M − $ArSO_2$), 155 ($MeC_6H_4SO_2$), 130 (*m/e* 177 − SMe).

Anal. Calcd for $C_{16}H_{16}N_2O_2S_2$: C, 57.81; H, 4.85; N, 8.43; S, 19.29. Found: C, 57.47; H, 5.22; N, 8.25; S, 19.32.

Rechromatography of the slowest band using five developments with CCl_4–acetone (82:18) separated 464 mg (17%) of unreacted **18a** from 293 mg (9%) of *N*-(2-cyano-6-methylthiomethylphenyl)-*p*-toluenesulfonamide (**20**): mp 125–128° from ether; λ_{max}^{MeOH} 222 mμ (sh, ε 28,200), 285 (sh, 1700); ν_{max} (KBr) 3300, 2240, 1635, 1600, 1585 cm^{-1}; nmr ($CDCl_3$) 1.89 (s, 3, SMe), 2.42 (s, 3, ArMe), 3.55 (s, 2, $ArCH_2S$), 7.5 ppm (m, 8, Ar and NH); mass spectrum (70 eV) *m/e* 332 (M^+), 177 (M − $MeC_6H_4SO_2$), 155 ($MeC_6H_4SO_2$), 131 (*m/e* 177 − SMe).

Anal. Calcd for $C_{16}H_{16}N_2O_2S_2$: C, 57.81; H, 4.85; N, 8.43; S, 19.29. Found: C, 57.83; H, 5.02; N, 8.25; S, 19.20.

Reaction of *N*-(2-Nitrophenyl)-*p*-toluenesulfonamide (18b).—A solution of **18b** (2.92 g, 10 mmol), DCC (6.18 g, 30 mmol), and anhydrous phosphoric acid (5 mmol) in DMSO (10 ml) and benzene (5 ml) was kept for 3 days at room temperature. After dilution with ether, filtration, and three extractions with water, the solution was extracted four times with 1 *N* sodium hydroxide. Acidification of the extracts and extraction with chloroform gave 0.79 g of relatively pure unreacted **18b**. Preparative tlc of the alkali insoluble fraction using three developments with hexane–ether (3:2) gave two products. Elution of the major, slower band gave 1.90 g (54%) of *N*-(2-nitrophenyl)-*N*-methylthiomethyl-*p*-toluenesulfonamide (**19c**) as a very viscous yellow syrup. An analytical sample could be distilled in a Kugelrohr apparatus[22] at 150° (10^{-3} mm): λ_{max}^{MeOH} 227 mμ (ε 17,400); ν_{max} (KBr) 1605, 1550, 1175 cm^{-1}; nmr ($CDCl_3$) 2.20 (s, 3, SMe), 2.41 (s, 3, ArMe), 4.87 (s, 2, NCH_2S), 7.1–7.9 ppm (m, 8, Ar).

Anal. Calcd for $C_{15}H_{16}N_2O_4S_2$: C, 51.14; H, 4.58; N, 7.95. Found: C, 51.47; H, 4.72; N, 7.71.

Elution of the faster and gave 355 mg (8%) of *N*-(methylthiomethyl)-*N*-(2-methylthiomethyl-6-nitrophenyl)-*p*-toluenesulfonamide (**19d**) as a viscous syrup: λ_{max}^{MeOH} 225 mμ (sh, ε 18,500); ν_{max} (KBr) 1600, 1535 cm^{-1}; nmr ($CDCl_3$) 2.12 (s, 3, SMe), 2.20 (s, 3, SMe), 2.42 (s, 3, ArMe), 3.77 and 4.15 (d, 1, J_{gem} = 14 Hz, $ArCH_2S$), 4.74 and 5.17 (d, 1, J_{gem} = 14 Hz, NCH_2S), 7.1–8 ppm (m, 7, Ar).

Anal. Calcd for $C_{17}H_{20}N_2O_4S_3$: C, 49.51; H, 4.89; N, 6.79. Found: C, 49.86; H, 4.97; N, 6.61.

***N*,*N*-Di-*p*-Toluenesulfonyl-2,6-dichloroaniline.**—A solution of 2,6-dichloroaniline (8.1 g, 50 mmol) and *p*-toluenesulfonyl chloride (10.0 g, 53 mmol) in pyridine (30 ml) was heated under reflux for 2 days. After evaporation of the solvent the residue was triturated with aqueous methanol (1:1) giving 7.8 g (67%) of *N*,*N*-di-*p*-toluenesulfonyl-2,6-dichloroaniline: mp 252–255° (raised to 256–258° upon recrystallization from chloroform–methanol); ν_{max} (KBr) 1600, 1570, 1495, 1440 cm^{-1}; nmr ($CDCl_3$) 2.46 (s, 6, ArMe), 7.32 (m, 7, Ar), 7.95 (d, 4, J = 8 Hz, Ar).

Anal. Calcd for $C_{20}H_{17}NO_4S_2Cl_2$: C, 51.07; H, 3.64; N, 2.98; S, 13.63. Found: C, 50.95; H, 3.67; N, 3.04; S, 13.64.

***N*-(1,3-Dicyclohexylformamidin-2-yl)saccharin (22).**—Saccharin (1.83 g, 10 mmol) and DCC (2.26 g, 11 mmol) were dissolved in ethyl acetate (5 ml) with gentle warming. After a few minutes crystals began to separate and after 16 hr the mixture was diluted with hexane and filtered. The crystals were washed with hexane and dried, leaving 4.0 g of **22** contaminated with only a trace of dicyclohexylurea. Recrystallization from methanol gave 3.62 g (93%) of pure **22**: mp 200–201°; λ_{max}^{MeOH} 225 mμ (ε 21,700); ν_{max} (KBr) 3310, 1665, 1570 cm^{-1}; nmr ($CDCl_3$) 0.9–2.5 (m, 20, cyclohexyl), 3.8 and 4.5 (m, 1, >CHN), 5.38 (d, 1, $J_{H,NH}$ = 7 NH), 7.5–8.0 ppm (m, 4, Ar); mass spectrum (70 eV) *m/e* 389 (M^+), 308 (M − C_6H_9), 226 (M − $2C_6H_9$), 206 (DCC^+), 183 (M − HDCC).

Anal. Calcd for $C_{20}H_{27}N_3O_3S$: C, 61.68; H, 6.99; N, 10.79. Found: C, 61.48; H, 7.05; N, 10.53.

Registry No.—**2**, 29494-72-2; **4a**, 31657-44-7; **4b**, 31657-42-8; **4c**, 31657-43-9; **4d**, 31657-44-0; **5a**, 640-61-9; **5b**, 1576-37-0; **6**, 31657-47-3; **8a**, 31657-48-4; **8b**, 1109-54-2; **9**, 31657-50-8; **10**, 68-34-8; **12a**, 31657-51-9; **12b**, 31657-52-0; **13**, 4703-15-5; **16**, 31657-54-2; **17**, 31657-55-3; **18a**, 31659-28-6; **18b**, 6380-13-8; **19a**, 31659-30-0; **19b**, 31659-31-1; **19c**, 31659-32-2; **19d**, 31659-33-3; **20**, 31659-34-4; **22**, 31659-33-5; ammonium *p*-toluenesulfonate, 4124-42-9; *N*,*N*-di-*p*-toluenesulfonyl-2,6-dichloroaniline, 31659-37-7; DMSO, 67-68-5.

(22) R. Graeve and G. H. Wahl, *J. Chem. Educ.*, **41**, 279 (1964).

Addition of Sulfonyl Chlorides to Acetylenes. I. Stereoselective Syntheses of β-Chlorovinyl Sulfones[1]

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The copper-catalyzed addition of sulfonyl chlorides to acetylenes makes possible the one-step syntheses of β-chlorovinyl sulfones in high yields. The stereoselective 1:1 addition apparently takes place by a free-radical chain reaction in which the copper catalyst functions as a chlorine atom transfer agent. The stereochemical course of the addition and configurational assignments of the isomeric adducts are discussed. Addition products of aryl-, methane-, and chloromethanesulfonyl chlorides and phenylacetylene, terminal alkynes (1-hexyne and 1-octyne), nonterminal alkyne (3-hexyne), and diphenylacetylene are described.

This paper presents examples of 1:1 additions of sulfonyl chlorides across the triple bond yielding β-chlorovinyl sulfones in high yields; these examples describe the addition of an arylsulfonyl chloride (R = C_6H_5) and alkylsulfonyl chlorides (R = CH_3, $ClCH_2$) to phenylacetylene, 1-hexyne, 1-octyne, and 3-hexyne, as well as the addition of *p*-toluenesulfonyl chloride to diphenylacetylene.[2]

$$RSO_2Cl + R'C{\equiv}CR'' \longrightarrow RSO_2CR'{=}CClR''$$

R = C_6H_5, *p*-$CH_3C_6H_4$, CH_3, ClCH

R′ = H, C_2H_5;

R″ = C_6H_5, C_2H_5, *n*-C_4H_9, *n*-C_6H_{13}

The known synthetic routes leading to β-chlorovinyl sulfones are usually based on at least two steps. Typically, step 1 involves (a) nucleophilic addition of a

(1) Presented before the Second Organic Sulphur Symposium, Groningen, The Netherlands, May 1966; Y. Amiel, *Tetrahedron Lett.*, 661 (1971).

(2) After this paper was submitted for publication, W. E. Truce, C. T. Goralski, L. W. Christensen, and R. H. Bavry, *J. Org. Chem.*, **35**, 4217 (1970), described the addition of benzenesulfonyl chloride to phenylacetylene, giving a monoadduct of an unknown configuration, whereas treatment of benzenesulfonyl chloride with diphenylacetylene resulted only in recovered diphenylacetylene.

thiol[3] or a thiophenol[4] to a chloroacetylene and

$$RSH + R'C{\equiv}CCl \longrightarrow \underset{\mathbf{1a}}{RSCR'{=}CHCl}$$

(b) addition of a sulfenyl chloride to an acetylene.[5]

$$RSCl + HC{\equiv}CR' \longrightarrow \underset{\mathbf{1b}}{RSCH{=}CClR'}$$

In step 2, the β-chlorovinyl sulfide (**1a** or **1b**) is subsequently oxidized to the corresponding sulfone.[6] Many of these thiols or sulfenyl chlorides are produced from the corresponding sulfonyl chlorides *via* reduction.[7] Therefore, the synthesis of β-chlorovinyl sulfones by a direct one-step addition reaction represents a distinct advance over previous syntheses.

Results and Discussion

The addition of sulfonyl chloride to the acetylenic bond takes place, in substantially homogenous solutions, by catalysis of copper(I) or copper(II) salts, under similar conditions as described for the free-radical addition of sulfonyl chlorides to olefins.[8] In the absence of catalyst no adduct formation was observed.[9] The reaction may be conducted with equimolar amounts of the reactants,[10] at reflux temperatures or preferably in a sealed tube, where rates of reaction could be conveniently followed by dilatometry. The reaction in a sealed tube proved to be much cleaner and faster, particularly when degassing removed atmospheric oxygen which resulted in decreased induction periods. The fact that the addition of the RSO_2 moiety occurred at the terminal carbon atom of terminal acetylenes, as in the case of terminal olefins,[8,11] strongly indicated the free-radical nature of the addition to acetylenes.

$$RSO_2Cl \longrightarrow RSO_2\cdot \quad (1)$$

$$RSO_2\cdot + HC{\equiv}CR' \longrightarrow RSO_2CH{=}\dot{C}R' \quad (2)$$

$$RSO_2CH{=}\dot{C}R' + RSO_2Cl \longrightarrow RSO_2CH{=}CClR' + RSO_2\cdot \quad (3)$$

Analogously when benzenesulfonyl chlorides and phenylacetylene were made to react in the presence of benzoyl peroxide, only telomeric sulfones were obtained, even in the presence of a large excess of sulfonyl chloride. However, the use of copper catalyst prevented telomerization and only 1:1 adducts were obtained.

In the copper chloride catalyzed addition of sulfonyl chlorides to vinylic monomers and other olefins, Asscher and Vofsi[8] suggested a redox-transfer mechanism; they proposed that the catalyst participated in every single cycle of the chain propagation as a chlorine atom transfer agent. In its oxidized form the copper catalyst is a much more reactive chlorine donor than the covalently bound chlorine of sulfonyl chloride. According to that mechanism the relatively slow transfer step, which is observed in a conventional process, is completely superseded in the presence of this catalyst by very fast reduction–oxidation steps. Likewise, it is suggested that a redox-transfer mechanism operates under similar conditions for the addition of sulfonyl radicals to acetylenes. Hence, step 3 is to be replaced by the two following successive steps, 4 and 5. Cupric

$$RSO_2CH{=}\dot{C}R' + CuCl_2 \longrightarrow RSO_2CH{=}CClR' + CuCl \quad (4)$$

$$CuCl + RSO_2Cl \rightleftharpoons CuCl_2 + RSO_2\cdot \quad (5)$$

chloride is known to be an efficient radical scavenger.[12] Step 4 represents an example of a well-studied ligand-transfer reaction[13] taking place on a vinyl radical. Few copper and iron salts catalyzed addition reactions to acetylenes are described to proceed in the ligand shell of the metal ion.[14] In step 5 other copper salts were found to generate sulfonyl radicals.[15] In cases where cupric ion catalysts were applied, a minute quantity of Cu(II) is reduced to Cu(I) while phenylacetylene is chlorinated.

It is interesting to note that, in these redox catalysis reactions conducted in the presence of ammonium, cuprous, and cupric chlorides, no oxidative coupling products of terminal acetylenes were formed. Moreover, an attempted oxidative coupling of phenylacetylene itself under these conditions did not take place. It seems that the described conditions favor a ligand-transfer process whereas a one-electron transfer is unfavorable for an oxidative coupling reaction.[16]

The stereochemical course of this addition reaction was investigated and was based mainly on the configurational proof of the carefully isolated adducts. Preliminary experiments of the copper-catalyzed reaction of benzenesulfonyl chloride with phenylacetylene in acetonitrile, in the presence of triethylammonium chloride,[17] gave high yields of a crystalline 1:1 addition product. Chromatographic separations revealed the presence of another compound; that this was an isomer of the main product was shown by elemental analysis, and catalytic reduction which gave the same known 2-phenylethyl phenyl sulfone.[18] The yield of adduct, mp 80°, was 72% and of the isomer, mp 84°, was 12%. Comparison of molecular models of these stereoisomers shows quite distinct differences. The cis addition product can accommodate a coplanar configuration, as shown in structure **3**, while the trans addition product (**2**) cannot attain coplanarity due to steric hindrance. In this configuration the *C*-phenyl group is apparently forced out of coplanarity and free rotation of this benzene ring is inhibited by the bulky sulfone group as

(3) L. I. Zakharkin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 437 (1959).

(4) W. E. Truce, M. M. Boudakian, R. F. Heine, and R. J. McManimie, *J. Amer. Chem. Soc.*, **78**, 2743 (1956); L. Maioli and G. Modena, *Bull. Sci. Fac. Chim. Ind. Bologna*, **16**, 86 (1958).

(5) F. Montanari, *Gazz. Chim. Ital.*, **86**, 406, 735 (1956); N. Kharasch and C. N. Yiannios, *J. Org. Chem.*, **29**, 1190 (1964), and preceding papers; N. Kharasch, Z. S. Ariyan, and A. J. Havlik, *Quart. Rep. Sulfur Chem.*, **1**, 93 (1966); V. Caló, G. Scorrano, and G. Modena, *J. Org. Chem.*, **34**, 2020 (1969), and preceding papers.

(6) A. Schöberl and A. Wagner, "Methoden der Organischen Chemie," Vol. IX, 4th ed, Houben-Weyl, Ed., Georg Thieme, Stuttgart, 1955, p 227.

(7) R. Adams and C. S. Marvel, "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 1941, p 504.

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

(9) The only reported example of addition of a sulfonyl halide to an acetylene involved *p*-toluenesulfonyl iodide and phenylacetylene; see W. E. Truce and G. C. Wolf, *Chem. Commun.*, 150 (1969).

(10) Usually a slight excess of phenylacetylene was used; a minute amount, as discussed later, was chlorinated.

(11) M. S. Kharasch and R. A. Mosher, *J. Org. Chem.*, **17**, 453 (1952); F. W. Stacey and J. F. Harris, Jr., *Org. React.*, **13**, 200 (1963).

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

(13) D. C. Nonhebel and W. A. Waters, *Proc. Roy. Soc., Ser. A*, **242**, 16 (1957); J. K. Kochi, *Science*, **155**, 415 (1967).

(14) A. V. Dombrovski, *Zh. Obshch. Khim.*, **27**, 3050 (1957); F. Minisci and R. Galli, *Tetrahedron Lett.*, 1679 (1965).

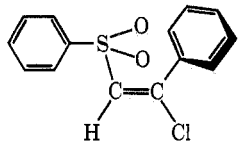
(15) To be published in a forthcoming paper.

(16) W. Eglinton and W. McCrea, *Advan. Org. Chem.*, **4**, 225 (1963).

(17) A quaternary ammonium chloride was used in these reactions for various reasons,[8] such as an aid to solubilize the copper salts through complex formation. This phenomenon is investigated further in a forthcoming publication.

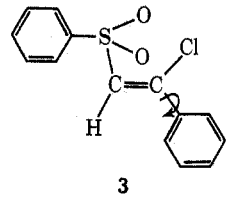
(18) T. Posner, *Ber.*, **38**, 651 (1905).

shown in structure **2** and interference in resonance stabilization would be anticipated. The ultraviolet spectrum of the described main product, melting at 80°, had an absorption in the styryl band region at 262 mμ (ε 10,000) while the absorption of the minor isomeric adduct was observed at 275 mμ (ε 20,000). It is obvious by these data that the adduct **3** has a higher degree of conjugation resulting from planarity in the styryl moiety. The configurational assignment of **2** and **3** to the main and minor addition products, respectively was based upon the ultraviolet spectra.



2

trans addition
(main) product



3

cis addition
(minor) product

Further evidence supporting the above-stated configurational assignments was based on dehydrochlorination reactions of **2** and **3**. Adduct **2** was recovered unchanged and in almost quantitative yield despite prolonged heating with a tertiary amine. However, **3** was so readily dehydrochlorinated that the known phenylethynyl phenyl sulfone[19] was obtained by merely eluting the dissolved adduct on a basic chromatographic column. It is known that β-elimination reactions of halo olefins to form acetylenes proceed best when the elements to be eliminated are located trans to each other.[20]

The reactions described in this paper represent a stereoselective addition reaction affording, in high yields, probably the kinetic-preferred, trans addition product as a result of a trans addition process. Trans additions to acetylenes are more frequently observed,[21,22] although cis additions have been occasionally mentioned, particularly in a few ionic,[23] photochemical,[24] and heterogeneous phase[25] addition reactions. The "trans addition rule" proposed by Truce and Simms[21] for the nucleophilic addition of thiols to phenylacetylene has been well accepted; the same stereochemical course of addition was described to take place by a free-radical chain mechanism to give the less stable cis vinylic sulfides, which were readily isomerized by an excess of thiyl radicals.[26] The ionic and radical addition of sulfenyl chloride to acetylenes also occurs, in general, in a trans fashion.[5,27]

(19) W. E. Truce, H. E. Hill, and M. M. Boudakian, *J. Amer. Chem. Soc.*, **78**, 2760 (1956).

(20) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, p 348.

(21) W. E. Truce and J. A. Simms, *J. Amer. Chem. Soc.*, **78**, 2756 (1956).

(22) S. I. Miller, *ibid.*, **78**, 6091 (1956).

(23) E. Winterfeldt in "Chemistry of Acetylenes," H. G. Viehe, Ed., Marcel Dekker, New York, N. Y., 1969, pp 275, 280, 294, 302, 313, 321.

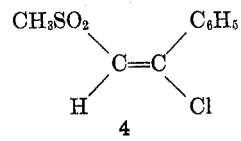
(24) L. D. Bergel'son, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1235 (1960).

(25) R. A. Benkeser and R. A. Hickner, *J. Amer. Chem. Soc.*, **80**, 5298 (1958).

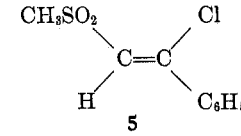
(26) N. Kharasch, S. J. Potempa, and H. L. Wehrmeister, *Chem. Rev.*, **39**, 269 (1946); A. A. Oswald, K. Griesbaum, B. E. Hudson, Jr., and J. M. Bregman, *J. Amer. Chem. Soc.*, **86**, 2877 (1964); A. A. Oswald and K. Griesbaum in "The Chemistry of Organic Sulfur Compounds," Vol. 2, N. Kharasch and C. Y. Meyers, Ed., Pergamon Press, Elmsford, N. Y., 1966, p 233; K. Griesbaum, *Angew. Chem., Int. Ed. Engl.*, **9**, 273 (1970).

(27) V. Caló, G. Modena, and G. Scorrano, *J. Chem. Soc. C*, 1339, 1344 (1968).

The addition of methanesulfonyl chloride to phenylacetylene, under described conditions, gave the trans addition product **4** in 65% yield. This alkylsulfonyl chloride was less reactive than benzenesulfonyl chloride and longer induction periods and reaction times were required. The isomeric adduct, **5**, was obtained in 10% yield by subjecting the reaction mixture to column chromatography.



4



5

Configurational assignments were based on the same criteria as for the previously described adducts. Additions of sulfonyl chlorides were also carried out with terminal and nonterminal alkynes, leading to the previously unknown β-chlorovinyl alkyl sulfones. Under the described conditions, addition products of benzenesulfonyl chloride with 1-hexyne and 1-octyne were synthesized.

$$C_6H_5SO_2Cl + HC{\equiv}CR \longrightarrow \underset{\mathbf{6}}{C_6H_5SO_2CH{=}CClR}$$

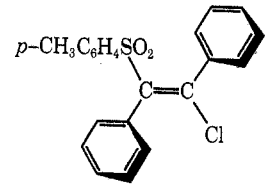
R = *n*-butyl, *n*-hexyl

Benzenesulfonyl chloride was added to a nonterminal alkyne, *e.g.*, 3-hexyne, under the same conditions.

$$C_6H_5SO_2Cl + CH_3CH_2C{\equiv}CCH_2CH_3 \longrightarrow \underset{\mathbf{7}}{\begin{matrix} C_6H_5SO_2 \\ \diagdown \\ \quad C{=}CClCH_2CH_3 \\ \diagup \\ CH_3CH_2 \end{matrix}}$$

Benzenesulfonyl chloride was also added to diphenylacetylene. After heating equimolar amounts of *p*-toluenesulfonyl chloride and diphenylacetylene, in the presence of cupric chloride and triethylammonium chloride in acetonitrile at 139° for 24 hr, 80% conversion (calculated on *p*-toluenesulfonyl chloride consumed) was obtained, whereas 15% of unreacted starting materials was recovered. The two isomeric adducts were separated by column chromatography giving a distribution of 53% of **8** and 47% of **9**. Compound **8** was pre-

$$p\text{-}CH_3C_6H_4SO_2Cl + C_6H_5C{\equiv}CC_6H_5 \longrightarrow$$



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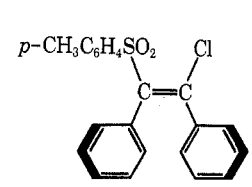


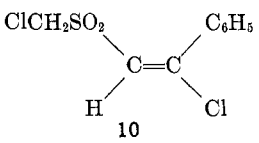
8 **9**

viously obtained by oxidation of the corresponding sulfide for which a trans configuration was postulated.[28] Structural assignments of **8** and **9** were based on spectral comparisons. Nmr spectra of the two isomeric adducts revealed that the methyl group in **9** was slightly deshielded as compared to **8**. A similar effect was observed in the nmr spectra of the two isomeric addition products of *p*-toluenesulfonyl chloride and phenyl-

(28) L. Di Nunno, G. Melloni, G. Modena, and G. Scorrano, *Tetrahedron Lett.*, 4405 (1965).

acetylene.[15] This resemblance supports the configurational assignment for both isomers. Neither **8** nor **9** can accommodate a coplanar configuration. The slight bathochromic shift shown by **9** suggested a somewhat better conjugation; molecular models tend to substantiate this.

To get some comparison of reactivity of sulfonyl radicals toward acetylenes and olefins, the additon of chloromethanesulfonyl chloride to phenylacetylene and 1-octyne was investigated. It has been reported previously[29] that this sulfonyl chloride decomposes with elimination of sulfur dioxide, and subsequent addition of chloromethyl radical to the olefin. Chloromethanesulfonyl chloride gave with phenylacetylene a 20% yield of the expected adduct (**10**), whereas, in the case of styrene, the corresponding addition product was obtained in 60% yield.[30]



10

Kharasch, *et al.*,[31] described phenylacetylene as being less reactive than styrene. On the other hand, it seems that sulfonyl radicals attack alkynes more readily than corresponding olefins. While the attempted copper-catalyzed addition of chloromethanesulfonyl chloride to 1-octene gave no adduct,[30] 1-octyne did lead to the expected adduct (**11**) in 6% yield.

$$ClCH_2SO_2Cl + HC{\equiv}C(CH_2)_5CH_3 \longrightarrow ClCH_2SO_2CH{=}CCl(CH_2)_5CH_3$$

11

Addition of benzenesulfonyl chloride to 1-hexyne and 1-hexene, under the same conditions, again indicated that the alkyne is a much more reactive substrate than the corresponding olefin. Thus, adduct formation (based on isolated product, yields calculated on total benzenesulfonyl chloride) after 2, 4, 8, 12, and 24 hr for 1-hexyne and 1-hexene were 30 *vs.* 6%, 44 *vs.* 14%, 60 *vs.* 28%, 67 *vs.* 36%, and 71 *vs.* 55%, respectively.

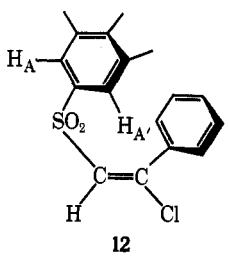
The simultaneous catalytic hydrogenation and hydrogenolysis of the alkynic adduct, as well as the catalytic hydrogenolysis of the alkenic adduct, gave the identical saturated sulfone. Similarly, **4**, **5**, and **10** gave the known 2-phenylethyl methyl sulfone.[21]

The alkynic addition products (**6**, **7**, and **11**), which were liquids, were purified by fractional distillation under reduced pressure; spectral data indicated a trans addition configuration, although presence of some cis addition products in the distillates could not be excluded.

In addition to very significant differences between the trans and cis addition products in the ultraviolet, the infrared spectra proved to be very useful in the identification of the isomeric adducts, particularly in the chromatographic separations. It was possible to characterize the structural isomers on the basis of sharp and strong –CH= out-of-plane bending vibrations at 11.05 and 10.76 μ of the trans addition products and at 10.72 and 10.92 μ of the cis addition products. Additional distinctions were also found in the C=C stretching frequencies region: at 6.19 μ for trans addition products and at 6.36 μ for corresponding isomers, apparently due to higher conjugation of the latter.

An nmr comparison of the stereoisomers showed that the vinylic proton of the cis addition products was more deshielded (**3**, δ 7.16; **5**, δ 7.15) than in the trans addition products (**2**, δ 6.98; **4**, 6.92; **10**, δ 6.87). This effect is evidently due to the location of the vinylic proton in **3** and **5** in the deshielding zone of the neighboring cis phenyl ring.[32]

Two phenyl protons of **2** and **3** were found to be more deshielded than the remaining eight aromatic protons present in the two phenyl rings. These protons, ortho to the carbon atom attached to the electronegative sulfone group, appeared in each case as a doublet, being more deshielded in **3** (δ 8.08, J = 8 Hz) than in **2** (δ 7.54, J = 5 Hz); this indicated a shielding effect in the latter due to the proximity in space of the two phenyl rings, in a displaced face-to-face conformation[33] (see **12**). A similar shielding effect of the phenyl ring on the methyl protons was noted in **4** (δ 2.73), as compared to **5** (δ 3.20). Such an effect was observed (*vide supra*) in **8** and **9**, to a much lesser extent, for the protons of the para-substituted methyl groups.



12

Experimental Section[34]

Materials.—Phenylacetylene and methanesulfonyl and benzenesulfonyl chlorides obtained from Fluka (puriss) were distilled before use; chloromethanesulfonyl chloride was prepared from trithiane by chlorinolysis in water;[35] 1-hexyne, bp 71–72°, was synthesized from *n*-butyl bromide and sodium acetylide in liquid ammonia;[36] 1-octyne, bp 76–77° (150 mm), was synthesized in a similar way; 3-hexyne was obtained from Colombia Organic Chemicals Co.; diphenylacetylene was prepared according to the literature;[37] anhydrous cuprous chloride (pract) was obtained from Fluka; 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 isopropyl alcohol and dried at 100°; acetonitrile from Fluka (puriss) was dried over P_2O_5; benzoyl peroxide was obtained from Fisher, Florisil, 100–200 mesh, was obtained from Floridin Co.; and silica gel (Kieselgel H) was obtained from Merck.

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(32) D. R. Davis and J. D. Roberts, *J. Amer. Chem. Soc.*, **84**, 2252 (1962); NMR Spectra Catalog, Varian Associates, Palo Alto, Calif., 1962, No. 232; Gurudata, J. B. Stothers, and J. D. Talman, *Can. J. Chem.*, **45**, 731 (1967).

(33) F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1960, pp 66–68.

(34) All melting points and boiling points are uncorrected. Ir spectra were determined in $CHCl_3$ on a Perkin-Elmer Infracord Model 237B spectrophotometer; uv spectra were obtained in aqueous C_2H_5OH on a Cary Model 14M spectrophotometer; nmr spectra were measured in $CDCl_3$ on a Varian A-60 instrument with TMS as internal standard and chemical shifts are reported in δ (ppm) units. Microanalyses were performed in our microanalytical section directed by Mr. R. Heller.

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(36) K. N. Campbell and B. K. Campbell, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 117.

(37) L. I. Smith and M. M. Falkof, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 350.

(*E,Z*)-**2-Benzenesulfonyl-1-chlorostyrene (2 and 3).**—A mixture of 8.8 g (50 mmol) of benzenesulfonyl chloride, 5.36 g (52.5 mmol) of phenylacetylene, 134 mg (1 mmol) of anhydrous cupric chloride, and 413 mg (3 mmol) of triethylammonium chloride in 3 g of acetonitrile was introduced into a Carius tube, cooled in liquid air, degassed (three times) at 0.1 mm, sealed, and heated for 3 hr at 100°. After a 10-min induction period the reaction began as indicated by the onset of contraction. Nearly 90% of reaction took place after 1.5 hr. After contraction stopped the tube was cooled in liquid air and then opened. The semisolid reaction mixture was dissolved in methylene chloride, transferred to a separatory funnel, and washed with water and an aqueous solution of disodium ethylenediaminetetraacetate until free from copper, and the organic layer was dried (Na_2SO_4). Evaporation of solvent gave 12.3 g of crude material which was subsequently crystallized from methanol to give 9.7 g (77% yield) of **2**: mp 80°; uv λ_{max} 212 mμ (ε 16,000) and 262 (10,000); ir 6.19, 6.27, 6.72, 6.92, 7.58, 7.65, 7.76, 8.62, 8.72, 9.25, 9.77, 10.02, 10.76, 11.05, and 12.3 μ; nmr δ 6.98 (s, 1 H, vinylic), 7.35–7.47 (m, 8 H, aromatic), 7.54 (d, 2 H, aromatic, J = 5 Hz).

Anal. Calcd for $C_{14}H_{11}ClO_2S$: C, 60.32; H, 3.97; S, 11.51; Cl, 12.72. Found: C, 60.49; H, 3.86; S, 11.53; Cl, 12.7.

A crude reaction mixture was chromatographed over 120 g of Florisil; elution with ether–*n*-hexane (1:3) gave 12 mg of the known diphenyl disulfide,[38] mp 61°.

Anal. Calcd. for $C_{12}H_{10}S_2$: C, 65.89; H, 4.72; S, 28.73. Found: C, 65.92; H, 4.70; S, 28.81.

The subsequent elution afforded 10 g (72%) of the above-described adduct, **2**. A further elution with ether–*n*-hexane (1:1) gave 1.67 g (12%) of **3**: mp 84° (methanol); uv λ_{max} 212 mμ (ε 15,500), 219 (15,500), and 275 (20,000); ir 6.28, 6.36, 6.72, 6.92, 7.22, 7.58, 7.65, 7.7, 8.1, 8.23, 8.5, 8.72, 9.22, 9.77, 10.01, 10.72, 10.92, and 12.2 μ; nmr δ 7.16 (s, 1 H, vinylic), 7.25–7.35 (m, 8 H, aromatic), and 8.08 (d, 2 H, aromatic, J = 8 Hz).

Anal. Calcd for $C_{14}H_{11}ClO_2S$: C, 60.32; H, 3.97; S, 11.51; Cl, 12.72. Found: C, 60.53; H, 3.86; S, 11.79; Cl, 12.88.

Before Florisil was applied, Al_2O_3 (Woelm activity II) was tried. On this adsorbent phenylethynyl phenyl sulfone,[19] mp 74.5° (methanol), was formed in small amounts and was eluted with ether–*n*-hexane (1:5): ir 4.62 (–C≡C–), 7.63 and 8.58 μ (–SO_2–).

Anal. Calcd for $C_{14}H_{10}O_2S$: C, 69.17; H, 4.03; S, 13.48. Found: C, 69.42; H, 4.16; S, 13.21.

An addition reaction was performed with the same reagent mixture under reflux conditions in a nitrogen atmosphere; the temperature of the reaction mixture was 96°. After 6 hr the reaction was worked up as described before. Benzenesulfonyl chloride (4.85 g) and phenylacetylene (3.2 g) were recovered and the crude material (4.8 g, 35% conversion) was chromatographed over Florisil, affording 4.0 g (60%) of **2** and 0.6 g (10%) of **3** (yields are based on reacted benzenesulfonyl chloride).

Catalytic Reduction of 2, 3, and Phenylethynyl Phenyl Sulfone.—Adducts **2**, **3**, and phenylethynyl phenyl sulfone were reduced with H_2 over 5% Pd/C in methanol at 25° and atmospheric pressure; in each of three reductions 2-phenylethyl phenyl sulfone,[18] mp 58–59° (ethanol), was obtained quantitatively. An attempted preferential hydrogenolysis did not work; hydrogenation of the double bond took place simultaneously.

Sodium Borohydride Reduction of 2 and 3.—Adducts **2** and **3** were reduced in diglyme at 25°; the same saturated 2-phenylethyl phenyl sulfone was obtained.

Addition Reaction of Benzenesulfonyl Chloride to Phenylacetylene in the Presence of Benzoyl Peroxide.—A mixture of 17.6 g (100 mmol) of benzenesulfonyl chloride, 2.04 g (20 mmol) of phenylacetylene, and 0.48 g (2 mmol) of benzoyl peroxide in 5 ml of methylene chloride was introduced into a Carius tube, cooled in liquid air, evacuated to 0.1 mm, degassed (three times), sealed, and heated for 2 hr at 100°. After a 25-min induction period the reaction began as indicated by volume contraction and color darkening. After 2 hr the tube was cooled in liquid air and then opened. Volatile fractions were distilled off under reduced pressure. Most of the reactants were recovered unchanged, leaving a viscous telomeric residue (0.98 g). Chromatographic separation over Florisil did not lead to any solid product. The ir of the various fractions showed typical sulfone absorptions (7.6 and 8.7 μ).

Attempted Oxidative Coupling of Phenylacetylene.—To determine if phenylacetylene would undergo an oxidative coupling reaction under the above-described redox conditions, a mixture of 1.02 g (10 mmol) of phenylacetylene, 0.3 g (3 mmol) of anhydrous cuprous chloride, 0.7 g (5 mmol) of anhydrous cupric chloride, and 1.38 g (10 mmol) of triethylammonium chloride in 3 g of acetonitrile was heated in a sealed tube, after prior degassing (three times), for 17 hr at 100°. After usual work-up, removal of unreacted phenylacetylene and volatile chlorinated products (having a density greater than water and giving a positive Beilstein test) under reduced pressure, a semisolid residue weighing 58 mg was obtained. From this, only 15 mg of diphenyl-α-diacetylene, mp 87.5°, was isolated; this was probably formed during the work-up process, which was done in the presence of air. A mixture melting point of 87.5° was obtained with an authentic sample prepared by oxidative coupling in the presence of air.

Attempted Dehydrochlorination of 2.—A solution of 1.39 g (5 mmol) of **2** and 1.11 g (6 mmol) of triethylamine in 3 ml of benzene was heated in a sealed tube for 20 hr at 100°. Only traces of triethylammonium chloride precipitating out in the solution were found. As a result of a chromatographic separation, 1.2 g (92%) of the starting material (**2**) was recovered.

(*E,Z*)-**2-Methanesulfonyl-1-chlorostyrene (4 and 5).**—The addition reaction and the work-up procedure were carried out as described for benzenesulfonyl chloride using 7.4 g (50 mmol) of methanesulfonyl chloride. After a 45-min induction period, 10 hr of reaction time was required. The crude material (7.9 g) was obtained by distillation, bp 128–133° (0.2 mm), as an oily material ($n^{22}D$ 1.588) which slowly solidified at room temperature and subsequently chromatographed over Florisil. Elution with ether–*n*-hexane (1:3) gave 6.5 g (65% yield) of **4**: mp 59–60° (methanol); uv λ_{max} 213 mμ (ε 8000) and 253 (8000); ir 6.18, 6.27, 6.72, 6.92, 7.1, 7.58, 7.65, 8.75, 10.35, 10.74, 11.02, and 12.2 μ; nmr δ 2.73 (s, 3 H, CH_3), 6.92 (s, 1 H, vinylic), and 7.45–7.65 (m, 5 H, aromatic).

Anal. Calcd for $C_9H_9ClO_2S$: C, 49.88; H, 4.17; S, 14.8; Cl, 16.36. Found: C, 49.94; H, 4.19; S, 14.72; Cl, 16.43.

Further elution with ether–*n*-hexane (1:1) of the same chromatogram afforded 2.15 g (10% yield) of **5**: mp 53.5–54° (methanol); uv λ_{max} 212 mμ (ε 8000) and 264 (16,000); ir 6.26, 6.36, 6.72, 6.92, 7.1, 7.58, 7.7, 8.75, 10.27, 10.72, 10.92, and 12.2 μ; nmr δ 3.20 (s, 3 H, CH_3), 7.15 (s, 1 H, vinylic), and 7.45–7.75 (m, 5 H, aromatic).

Anal. Calcd. for $C_9H_9ClO_2S$: C, 49.88; H, 4.17; S, 14.8; Cl, 16.36. Found: C, 49.85; H, 4.13; S, 14.91; Cl, 16.52.

1-Benzenesulfonyl-2-chloro-1-hexene (6, R = *n*-Butyl).—A mixture of 8.8 g (50 mmol) of benzenesulfonyl chloride, 4.52 g (55 mmol) of 1-hexyne, 134 mg (1 mmol) of cupric chloride, 413 mg (3 mmol) of triethylammonium chloride, and 3 g of acetonitrile was introduced into a Carius tube, cooled in liquid air, degassed three times at 0.1 mm, sealed, and heated at 100°. The reaction began after a 20-min induction period, as indicated by the onset of contraction, measured by dilatometry. After 16 hr, when contraction stopped, the tube was cooled in liquid air and then opened. The reaction mixture was transferred to a separatory funnel and washed with water and an aqueous solution of disodium ethylenediaminetetraacetate until free from copper, and the organic layer was dried (Na_2SO_4). Evaporation of solvent gave, after fractional distillation, 9.7 g (75%) of a colorless oil: bp 123–124° (0.17 mm); $n^{22}D$ 1.5452; mp 13–14° (methanol); ir (neat) 6.18, 6.25, 6.72, 6.82, 6.92, 7.22, 7.53, 7.63, 7.66, 7.82, 8.12–8.28, 8.47, 8.66, 8.88, 9.21, 9.77, 9.82, 10.0, 10.1, 10.25, 11.03, 11.5, 12.2, 13.3, 13.95, and 14.63 μ; nmr δ 0.95 (t, 3 H, CH_2CH_3), 1.48 (m, 4 H, $CH_2CH_2CH_2CH_2$), 2.97 (m, 2 H, $CClCH_2$), 6.55 (s, 1 H, vinylic), 7.5–8.07 (m, 5 H, aromatic).

Anal. Calcd for $C_{12}H_{15}ClO_2S$: C, 55.70; H, 12.39; Cl, 13.70; S, 12.39. Found: C, 56.00; H, 12.50; Cl, 13.78; S, 12.50.

By varying reaction time, under some conditions, the following yields of isolated addition product (calculated on total benzenesulfonyl chloride) were obtained: 30% (2 hr), 44% (4 hr), 60% (8 hr), 67% (12 hr), and 71% (24 hr).

Addition of Benzenesulfonyl Chloride to 1-Hexene.—The reaction was carried out in the same way as described above, using 1-hexene (4.52 g) instead of 1-hexyne. The reaction was followed by dilatometry. After 24 hr, contraction stopped, and

(38) This compound was also found in other reactions in which benzenesulfonyl radicals were involved; see J. L. Kice and N. E. Pawlowsky, *J. Amer. Chem. Soc.*, **86**, 4898 (1964); J. L. Kice and N. A. Favstritsky, *J. Org. Chem.*, **35**, 114 (1970); P. Koch, E. Ciuffarin, and A. Fava, *J. Amer. Chem. Soc.*, **92**, 5971 (1970).

the reaction mixture was worked up by the usual procedure to give 7.15 g (55%) of phenyl (2-chloro-*n*-hexyl) sulfone as a colorless oil by fractional distillation, bp 135–138° (0.2 mm), $n^{26}D$ 1.5265. This oil solidified at room temperature and was recrystallized from methanol: mp 33–34°; ir (neat) 6.29, 6.85, 6.92, 7.25, 7.53, 7.65, 7.82, 8.12, 8.68, 8.88, 9.22, 9.35, 9.78, 10.02, 10.27, 10.65, 11.2, 11.45, 11.8, 12.88, 13.5, and 14.63 μ.

Anal. Calcd for $C_{12}H_{17}ClO_2S$: C, 55.27; H, 6.57; Cl, 13.60; S, 12.30. Found: C, 55.38; H, 6.62; Cl, 13.30; S, 12.25.

By varying reaction time, under the same conditions, the following yields of isolated addition product (calculated on total benzenesulfonyl chloride) were obtained: 6% (2 hr), 14% (4 hr), 28% (8 hr), and 36% (12 hr).

1-Benzenesulfonyl-2-chloro-1-octene (6, R = *n*-Hexyl).—The reaction was carried out and worked up exactly as described in the above experiments, using 6.06 g (55 mmole) of 1-octyne instead of 1-hexyne, and 9.3 g (65%) of the adduct, in the form of a colorless oil, was obtained by fractional distillation: bp 144–148° (0.15 mm); $n^{22}D$ 1.5350; ir (neat) 6.18, 6.24, 6.72, 6.82, 6.92, 7.22, 7.52, 7.63, 8.06–8.26, 8.47, 8.66, 8.85, 9.21, 9.62, 10.0, 10.68, 11.15, 12.2, 13.3, 13.95, and 14.63 μ; nmr δ 0.87 (t, 3 H, CH_3), 1.35 [m, 8 H, $(CH_2)_4$], 2.95 (m, 2 H, $ClCH_2$), 6.57 (s, 1 H, vinylic), and 7.53–8.05 (m, 5 H, aromatic).

Anal. Calcd for $C_{14}H_{19}ClO_2S$: C, 58.62; H, 6.68; Cl, 12.36; S, 11.13. Found: C, 58.92; H, 6.73; Cl, 12.35; S, 11.56.

3-Benzenesulfonyl-4-chloro-3-hexene (7).—The reaction was carried out in the same way as described in the above experiments, using 3-hexyne instead of 1-hexyne, to give 7.75 g (60%) of the adduct, in the form of a colorless oil, as obtained by fractional distillation: bp 122–128° (0.2 mm); $n^{25}D$ 1.5628; ir (neat) 6.18, 6.78, 6.88, 6.92, 7.28, 7.55, 7.67, 8.65, 8.78, 9.25, 9.95, 10.6, 10.9, 12.15, 13.2, 13.6, and 14.6 μ; nmr δ 1.09 [t, 3 H, $C(Cl)CH_2\mathbf{CH_3}$, J = 5 Hz],[33] 1.12 [t, 3 H, $C(SO_2C_6H_5)CH_2\mathbf{CH_3}$, J = 5 Hz], 2.56 [q, 2 H, $C(Cl)\mathbf{CH_2}CH_3$, J = 7 Hz],[33] 3.04 [q, 2 H, $C(SO_2C_6H_5)\mathbf{CH_2}CH_3$, J = 7 Hz], and 7.5–8.0 (m, 5 H, aromatic).

Anal. Calcd for $C_{12}H_{15}ClO_2S$: C, 55.70; H, 5.84; Cl, 13.70; S, 12.39. Found: C, 55.31; H, 5.61; Cl, 13.36; S, 12.62.

Adducts of *p*-Toluenesulfonyl Chloride and Diphenylacetylene (8 and 9).—A mixture of 4.775 g (25 mmol) of *p*-toluenesulfonyl chloride, 4.456 g (25 mmol) of diphenylacetylene, 201 mg (1.5 mmol) of anhydrous cupric chloride, and 344 mg (2.5 mmol) of triethylammonium chloride in 4 g of acetonitrile was introduced into a Carius tube, cooled in liquid air, degassed (three times) at 0.1 mm, sealed, and heated for 20 hr at 139°. After the usual work-up, the residue (7.85 g) was subjected to column chromatography using silica gel (Kieselgel H, Merck), to which 5% of silver nitrate was impregnated and finally 2% of water was added. Elution with *n*-pentane afforded 0.625 mg (15%) of unreacted *p*-toluenesulfonyl chloride and 0.534 mg (12%) of unreacted diphenylacetylene; the solvent eluted *ca.* 40 mg of *trans*-dichlorostilbene, mp 143°, which had correct analysis and was compared with an authentic sample synthesized according to the literature.[39] Further elution gave the trans addition product (8), which was recrystallized from methanol, giving 3.33 g (53% of the adduct mixture): mp 142–143° (lit.[28] mp 140°); ir (KBr) 6.14, 6.26, 6.67, 6.93, 7.53, 7.63, 7.70, 7.73, 7.76, 7.82, 8.06, 8.37, 8.41, 8.43, 8.65, 8.92, 9.18, 9.28, 9.65, 9.78, 10.35, 10.90, 11.65, 12.26, 13.25, 13.5, 14.37, 14.5, 14.54, 14.8, and 15.53 μ; nmr δ 2.34 (s, 3 H, CH_3) and 7.1–7.95 (m, 14 H, aromatic).

Anal. Calcd for $C_{21}H_{17}ClO_2S$: C, 68.37; H, 4.65; Cl, 9.61; S, 8.69. Found: C, 68.62; H, 4.48; Cl, 9.48; S, 8.67.

(39) C. Davidson, *J. Amer. Chem. Soc.*, **40**, 397 (1918).

It was rather difficult to separate the mixture of the two adducts, and fractions containing mixtures were rechromatographed. Continued elutions afforded 2.95 g (47% of the adduct mixture) of the stereoisomeric adduct (9), obtained after crystallization from *n*-hexane in the form of plates: mp 153.5–154.5°; ir (KBr) 6.24, 6.27, 6.31, 6.35, 6.68, 6.92, 7.12, 7.22, 7.53, 7.63, 7.73, 7.95, 8.12, 8.38, 8.41, 8.58, 8.65, 9.18, 9.67, 9.77, 9.96, 10.25, 10.8, 11.75, 12.4, 13.1, 13.5, 14.4, and 14.7 μ; nmr δ 2.43 (s, 3 H, CH_3), 7.1–7.24 (m, 10 H, aromatic), 7.30 [d, 2 H, aromatic (meta to CSO_2),[15] J = 8.5 Hz], and 7.80 [d, 2 H, aromatic (ortho to CSO_2), J = 8.5 Hz].

Anal. Calcd. for $C_{21}H_{17}ClO_2S$: C, 68.37; H, 4.65; Cl, 9.61; S, 8.69. Found: C, 68.54; H, 4.66; Cl, 9.68; S, 8.64.

(*E*)-2-Chloromethanesulfonyl-1-chlorostyrene (10).—This addition reaction and work-up procedure was carried out as described for benzenesulfonyl chloride using 7.4 g (50 mmol) of chloromethanesulfonyl chloride. After 2.5 hr heating at 100° the tube was cooled in liquid air and then opened. Volatile material, including a relatively high volume of sulfur dioxide, was removed; no unreacted sulfonyl chloride remained. Distillation gave 0.45 g of a chlorinated olefinic liquid, probably 2-chloromethane-1-chlorostyrene, bp 95° (0.5 mm), and 2.5 g (20% yield) of 6, bp 138° (0.15 mm), which solidified and was crystallized from methanol: mp 51–52°; ir 6.18, 6.27, 6.72, 6.92, 7.22, 7.58, 7.72, 8.73, 10.73, 11.02, and 12.2 μ; nmr δ 4.21 (s, 2 H, CH_2), 6.87 (s, 1 H, vinylic), and 7.42–7.62 (m, 5 H, aromatic).

Anal. Calcd for $C_9H_8Cl_2O_2S$: C, 43.04; H, 3.21. Found: C, 42.86; H, 3.35.

Catalytic Reduction of 4, 5, and 10.—Adducts 4, 5, and 10 were reduced with H_2 over 5% Pd/C in methanol at 25° and atmospheric pressure; in each of the three reductions the known 2-phenylethyl methyl sulfone[21] was obtained quantitatively.

1-Chloromethanesulfonyl-2-chloro-1-octene (11).—The reaction was carried out in the same way as described in the first experiment, using 7.4 g (50 mmol) of chloromethanesulfonyl chloride and 6.06 g (55 mmole) of 1-octyne. After 2.5 hr the tube was cooled in liquid air and then opened. A relatively large amount of sulfur dioxide was found to be present in the reaction mixture, while no unreacted sulfonyl chloride remained. After removing the chlorinated olefinic liquid by distillation, there was obtained what is believed to be 1-chloromethyl-2-chloro-1-octene, bp 82–90° (0.2 mm). The desired adduct (11), 0.78 g (6%), was obtained as a colorless oil, at 132–136° (0.2 mm): ir ($CHCl_3$) 6.19, 6.57, 6.82, 6.97, 7.12, 7.22, 7.45, 7.87, 8.1, 8.7, 8.92, 9.52, 10.7, 11.4, 11.75, and 12.4 μ.

Anal. Calcd. for $C_9H_{16}Cl_2O_2S$: C, 41.70; H, 6.22. Found: C, 41.52; H, 6.38.

Catalytic Reduction of 6 (R = *n*-Butyl) and Phenyl (2-Chloro-*n*-hexyl) Sulfone (Addition Product of Benzenesulfonyl Chloride and 1-Hexene).—Simultaneous hydrogenation and hydrogenolysis of 6 (R = *n*-butyl) and hydrogenolysis of phenyl (2-chloro-*n*-hexyl) sulfone with H_2 over Pd/C in methanol at 25° and atmospheric pressure gave in each case the oily saturated sulfone; these two reduction products were compared by infrared (neat) giving identical spectra.

Registry No.—**2**, 31598-92-2; **3**, 31598-93-3; **4**, 20101-30-8; **5**, 31598-95-5; **6** (R = *n*-butyl), 31598-96-6; **6** (R = *n*-hexyl), 31598-97-7; **7**, 31598-98-8; **8**, 31598-99-9; **9**, 31599-00-5; **10**, 31599-01-6; **11**, 31599-02-7; benzenesulfonyl chloride, 98-09-9; phenylacetylene, 536-74-3; 1-hexene, 592-41-6; phenyl (2-chloro-*n*-hexyl) sulfone, 31662-29-0.