The Copper-Catalyzed Addition of Arenesulfonyl Chlorides to Conjugated Dienes, Trienes, and Phenylacetylene[1]

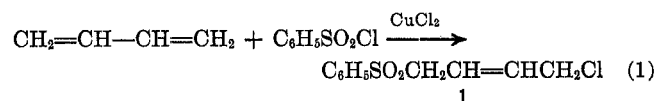William E. Truce, Christian T. Goralski, Larry W. Christensen, and Richard H. Bavry

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The copper-catalyzed addition of arenesulfonyl chlorides to 2-methyl-1,3-butadiene (isoprene), 1,3-cyclohexadiene, 1,3-cyclooctadiene, bicyclo[2.2.1]hepta-2,5-diene (norbornadiene), cycloheptatriene, and phenylacetylene to give 1:1 adducts is described. The adducts with 2-methyl-1,3-butadiene and 1,3-cyclohexadiene were dehydrohalogenated to the corresponding acyclic and cyclic 1,3-unsaturated sulfones, respectively.

The copper-catalyzed addition (Asscher–Vofsi reaction) of alkane- and arenesulfonyl chlorides to simple olefins[2] and substituted styrenes[3] has been described previously. This paper presents the results of our studies of the copper-catalyzed addition of arenesulfonyl chlorides to conjugated dienes and trienes.
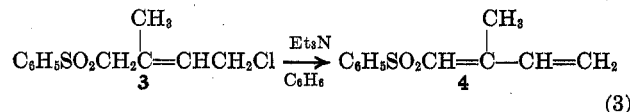
In their original paper, Asscher and Vofsi[2] reported that the reaction of benzenesulfonyl chloride with 1,3-butadiene gave the 1,4-monoadduct (**1,** eq 1). Similarly, we have found that treatment of 2-methyl-1,3-butadiene (**2**) with benzenesulfonyl chloride in the presence of cuprous chloride afforded a good yield of the 1,4 adduct **3** (eq 2). The stereochemistry about the
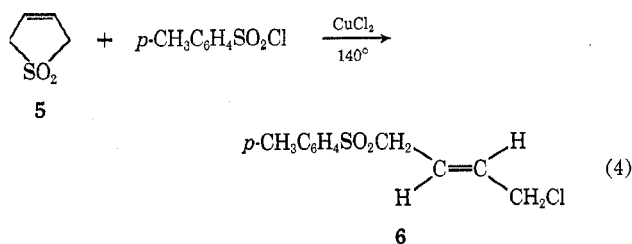
$$CH_2=CH-CH=CH_2 + C_6H_5SO_2Cl \xrightarrow{CuCl_2}$$
$$C_6H_5SO_2CH_2CH=CHCH_2Cl \quad (1)$$
$$\mathbf{1}$$
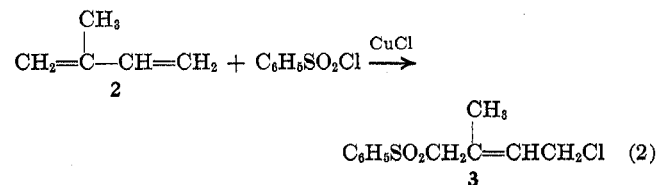
double bond in **3** is uncertain from the 100-MHz nmr spectrum.[4] Treatment of **3** with triethylamine in benzene resulted in dehydrohalogenation to the corresponding diene **4** in 93% yield (eq 3).

$$\underset{\mathbf{2}}{CH_2=\overset{\overset{\displaystyle CH_3}{|}}{C}-CH=CH_2} + C_6H_5SO_2Cl \xrightarrow{CuCl}$$
$$\underset{\mathbf{3}}{C_6H_5SO_2CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}=CHCH_2Cl} \quad (2)$$

$$\underset{\mathbf{3}}{C_6H_5SO_2CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}=CHCH_2Cl} \xrightarrow[C_6H_6]{Et_3N} \underset{\mathbf{4}}{C_6H_5SO_2CH=\overset{\overset{\displaystyle CH_3}{|}}{C}-CH=CH_2} \quad (3)$$

In continuing our investigations of free-radical additions to unsaturated sulfones,[5] the copper-catalyzed addition of benzenesulfonyl chloride to 3-sulfolene (**5**) was also studied. Treatment of **5** with benzenesulfonyl chloride for 2 hr at 108–110° under Asscher–Vofsi conditions resulted in no reaction. When the reaction was

repeated with *p*-toluenesulfonyl chloride at 135–140° a vigorous evolution of sulfur dioxide was observed, and the monoadduct with butadiene, 1-chloro-4-(*p*-toluenesulfonyl)-2-butene (**6**), was isolated in 67% yield (eq 4). In view of the known ability of 3-sulfo-

$$\underset{\mathbf{5}}{\overset{}{\text{(3-sulfolene)}}} + p\text{-}CH_3C_6H_4SO_2Cl \xrightarrow[140°]{CuCl_2}$$

$$\underset{\mathbf{6}}{p\text{-}CH_3C_6H_4SO_2CH_2}\overset{H}{\underset{H}{\diagdown}}C=C\overset{H}{\underset{CH_2Cl}{\diagup}} \quad (4)$$

lenes to serve as *in situ* sources of dienes,[6] it is reasonable to assume that butadiene was formed smoothly from 3-sulfolene (which itself is apparently inert to addition under these conditions) and subsequently underwent addition of *p*-toluenesulfonyl chloride to give **6.** The use of 3-sulfolenes as an *in situ* source of dienes in the Asscher–Vofsi reaction thus represents a convenient laboratory method of obtaining 1-chloro-4-(arenesulfonyl)-2-butenes, and avoids the need for employing sealed tube or bomb reactions with the highly volatile dienes.

The reaction of sulfonyl chlorides with cyclic conjugated dienes was also investigated. Reaction of benzenesulfonyl chloride with 1,3-cyclohexadiene afforded the 1,4 monoadduct **7** (eq 5). The 100-MHz nmr spec-

$$\underset{}{\text{(1,3-cyclohexadiene)}} + C_6H_5SO_2Cl \xrightarrow{CuCl} \underset{\mathbf{7}}{\overset{}{\text{(product 7)}}} \quad (5)$$
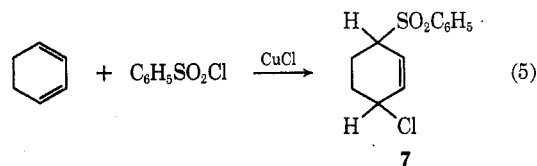
trum of **7** is consistent with a time average conformation in which both substituents are equatorial, indicating a trans addition of the sulfonyl chloride, and in which the molecule is in the half-chair conformation.[4] Treatment of **7** with triethylamine in benzene gave an

(1) Paper I in the series, Unsaturated Sulfones and Suitable Precursors.
(2) M. Asscher and D. Vofsi, *J. Chem. Soc.*, 4962 (1964).
(3) C. T. Goralski, Ph.D. Thesis, Purdue University, 1969.
(4) We gratefully acknowledge and thank Dr. Thomas E. Evans of the Chemical Physics Research Laboratory, The Dow Chemical Co., Midland, Mich., for determining and interpreting the 100-MHz nmr spectra.
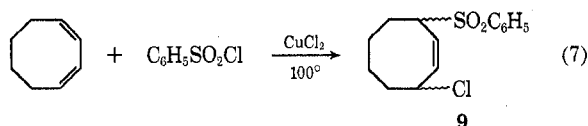(5) R. H. Bavry, Ph.D. Thesis, Purdue University, 1969.

(6) Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol. 9, Georg Thieme Verlag, Stuttgart, 1955, p 237.

excellent yield of 1-(benzenesulfonyl)cyclohexa-1,3-diene (8, eq 6). Thus the reactions outlined in eq 5 and
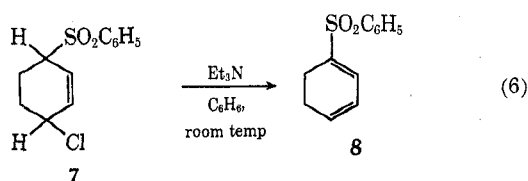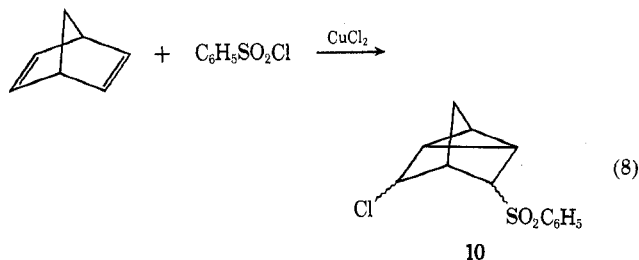

6 represent an excellent route to the novel, and previously unknown, cyclic 1,3-dienic sulfones.

Reaction of benzenesulfonyl chloride with 1,3-cyclooctadiene gave a 62% yield of a mixture of isomeric 1,4-addition products 9 (eq 7). The 100-MHz spec-
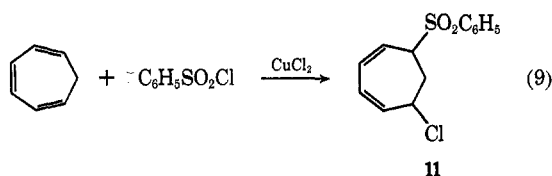

trum of 9 verified the presence of two isomeric 1,4-addition products in relative amounts of 70 and 30% but definite structures could not be assigned to the isomers.

The copper-catalyzed addition of sulfonyl chlorides was also investigated with a nonconjugated diene. Reaction of, benzenesulfonyl chloride with bicyclo-[2.2.1]hepta-2,5-diene gave a 21% yield of 5-chloro-3-nortricyclyl phenyl sulfone (10, eq 8).[7] The stereo-

chemistry of 10 could not be determined (100-MHz nmr) because of the high degree of symmetry of the hydrogens geminal to the chlorine and benzenesulfonyl substituents with respect to adjacent protons in the molecule.[4]

The reaction was extended to also include cyclic, conjugated trienes. The reaction of benzenesulfonyl chloride with cycloheptatriene afforded a 1:1 adduct 11 (eq 9). The 100-MHz nmr spectrum of 11 is consis-


tent with a time average conformation in which the benzenesulfonyl group is equatorial and the chlorine is

axial,[4] demonstrating that the adduct is the result of a trans 1,6 addition.[8]

The reaction of arylacetylenes with benzenesulfonyl chloride was also investigated.[9] Benzenesulfonyl chloride was found to react with phenylacetylene to give a monoadduct 12 (eq 10). The configuration of 12 is
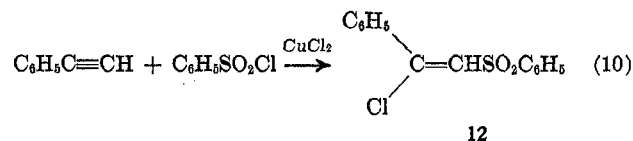

unknown (however, many free-radical reactions involving phenylacetylene proceed through a trans addition process).[10] Treatment of benzenesulfonyl chloride with diphenylacetylene resulted only in recovered diphenylacetylene.[11]

Experimental Section[12-14]

1-(Benzenesulfonyl)-2-methyl-4-chloro-2-butene.—A mixture of 14.9 g (0.0846 mol) of benzenesulfonyl chloride, 5.76 g (0.0846

(8) The observed product stereochemistry seems to indicate a mechanism in which the benzenesulfonyl group enters axially (perpendicular to the triene ring), the resulting intermediate radical undergoes a ring flip (placing the benzenesulfonyl group in the equatorial position), and, finally, the chlorine (via redox transfer) enters axially from the least hindered side.
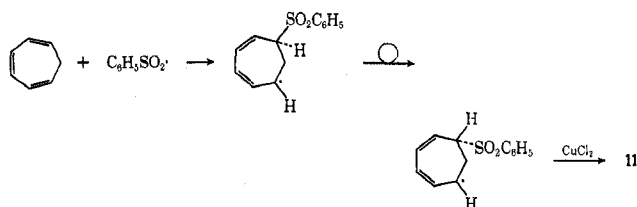
(9) Similar results were recently reported in the addition of benzenesulfonyl iodide to phenylacetylene: W. E. Truce and G. C. Wolf, *Chem. Commun.*, 150 (1969). The reaction of sulfonyl chlorides with substituted acetylenes has been briefly reported previously, but no details have ever been published: Y. Amiel, Abstracts of Papers, Second Organic Sulfur Symposium, Groningen, The Netherlands, 1966.

(10) The free-radical addition of thiols to phenylacetylene is a trans addition giving rise to cis products [A. A. Oswald, K. Griesbaum, B. E. Hudson, Jr., and J. M. Bregman, *J. Amer. Chem. Soc.*, **86**, 2877 (1964)], although the stereochemical course of the addition is highly dependent upon the relative amounts of the reactants. Addition of benzenethiol to a 20-fold excess of phenylacetylene yielded a mixture containing 95% of the corresponding cis monoadduct, while a 20-fold excess of the thiol led to the equilibrium mixture containing only 16% of cis isomer. It has been demonstrated that thiols, especially aromatic thiols, effectively catalyze the isomerization of the cis monoadducts, accounting for the above results. For a more detailed discussion of this topic, see A. A. Oswald and K. Griesbaum in "The Chemistry of Organic Sulfur Compounds," Vol. 2, N. Kharasch and C. Y. Meyers, Ed., Pergamon Press, New York, N. Y., 1966.

(11) In contrast, p-toluenesulfonyl iodide reacts with diphenylacetylene to give a 1:1 adduct in 35% yield: W. E. Truce and G. C. Wolf, *Chem. Commun.*, 150 (1969).

(12) All reactions were carried out in a nitrogen atmosphere. The cuprous chloride was reagent grade. The cupric chloride was reagent grade, and was dried at 140° prior to use. The 60-MHz nmr spectra were recorded on a Varian A-60A spectrometer with tetramethylsilane as an internal standard (TMS = 0). The 100-MHz spectra (in CDCl₃) were recorded on a Varian HA-100 spectrometer with an internal lock on tetramethylsilane (see ref 4). All melting points are uncorrected. The elemental analyses were performed by Dr. C. S. Yeh and the staff of the Purdue Microanalytical Laboratory.

(13) Asscher and Vofsi (ref 2) found that cuprous chloride and cupric chloride gave identical results with unconjugated olefins and vinylic monomers. Iron(II or III) chloride was found to be much less effective, giving only very poor yields of adduct. A free-radical mechanism was suggested for the reaction in which the copper catalyst participates in the propagation as a chlorine atom transfer agent (redox–transfer).

(14) Acetonitrile functions as a cosolvent for the copper catalyst. Kochi [*J. Amer. Chem. Soc.*, **77**, 5274 (1955); **84**, 2121 (1962)] has reported that the solubility of cupric chloride in acetonitrile is greatly enhanced by lithium chloride. It appears reasonable to suspect that in the system under consideration in this paper the copper catalyst exists as a higher halide complex of cupric ion ([CuCl₄²⁻][Et₃NH⁺]₂), as reported by Whealy, Bier, and McCormick [*J. Amer. Chem. Soc.*, **81**, 5900 (1959)], which has greater solubility than cupric chloride in organic solvents.

(7) S. J. Cristol and D. I. Davies, *J. Org. Chem.*, **29**, 1282 (1964); these authors reported the preparation of **10** in 7.3% yield via the peroxide-catalyzed addition of benzenesulfonyl chloride to bicyclo[2.2.1]hepta-2,5-diene.

mol) of 2-methyl-1,3-butadiene, 0.083 g (0.846 mmol) of cuprous chloride, 0.175 g (1.27 mmol) of triethylamine hydrochloride, and 3.4 g (0.079 mol) of acetonitrile was heated at reflux for 2 hr, cooled, and poured into 34 ml of cold methanol. A solid precipitated which was filtered, dried, and recrystallized from 95% ethanol to give 8.68 g (42% yield) of 1-(benzenesulfonyl)-2-methyl-4-chloro-2-butene: mp 72.5–73.5°; nmr (60 MHz, CDCl₃) δ 1.88 (s, 3), 3.80 (s, 2), 3.98 (d, 2), 5.37 (t, 1), and 7.76 (m, 5).

Anal. Calcd for C₁₁H₁₃ClO₂S: C, 54.00; H, 5.35; Cl, 14.50; S, 13.07. Found: C, 53.82; H, 5.30; Cl, 14.78; S, 13.10.

1-(Benzenesulfonyl)-2-methyl-1,3-butadiene.—To 50 ml of benzene at 0° containing 7.35 g (0.03 mol) of 1-(benzenesulfonyl)-2-methyl-4-chloro-2-butene was added 5.05 g (0.05 mol) of triethylamine. After stirring at room temperature for 24 hr, the reaction mixture was filtered and the benzene was removed *in vacuo* leaving a white solid. The solid was recrystallized from 75% ethanol to give 5.51 g (93% yield) of 1-(benzenesulfonyl)-2-methyl-1,3-butadiene: mp 68.5–69.5°; nmr (60 MHz, CDCl₃) δ 2.00 (s, 3), 5.65 (m, 2), 6.21 (m, 1), and 7.70 (m, 6).

Anal. Calcd for C₁₁H₁₂O₂S: C, 63.55; H, 5.85; S, 15.30. Found: C, 63.62; H, 5.71; S, 15.29.

Attempted Reaction of 3-Sulfolene with Benzenesulfonyl Chloride.—A mixture of 11.8 g (0.1 mol) of 3-sulfolene, 17.65 g (0.1 mol) of benzenesulfonyl chloride, 0.130 g (1.0 mmol) of cupric chloride, 0.206 g (1.5 mmol) of triethylamine hydrochloride, and 4 ml of acetonitrile was heated at 108–110° for 1.5 hr with stirring. The resultant dark orange reaction mixture was cooled to room temperature and 10 ml of methanol was added. After standing under refrigeration overnight, the methanol solution yielded a white, crystalline solid which was filtered and dried to give 8.3 g (71% recovery) of the starting 3-sulfolene, mp 64–66°.

1-(*p*-Toluenesulfonyl)-4-chloro-2-butene.—A mixture of 118 g (1.0 mol) of 3-sulfolene, 95.2 g (0.5 mol) of *p*-toluenesulfonyl chloride, 0.670 g (5 mmol) of cupric chloride, 1.03 g (8 mmol) of triethylamine hydrochloride, and 26 ml of acetonitrile was heated at 135–140° for 7.5 hr with stirring. The dark red reaction mixture was then cooled to room temperature, and the solid which separated was filtered and recrystallized twice from 95% ethanol to give 82.0 g (67% yield) of 1-(*p*-toluenesulfonyl)-4-chloro-2-butene, mp 69.5–71°. (*Caution:* This reaction should be run in a well-ventilated hood because a vigorous evolution of sulfur dioxide occurs as the reaction proceeds.)

Anal. Calcd for C₁₁H₁₃ClO₂S: C, 53.99; H, 5.35; mol wt, 244.7. Found: C, 53.93; H, 5.40; mol wt, 239.9 (acetone).

3-(Benzenesulfonyl)-6-chlorocyclohexene.—In a 100-ml, three-neck flask were placed 9.21 (0.0846 mol) of 1,3-cyclohexadiene, 14.9 g (0.084 mol) of benzenesulfonyl chloride, 0.083 g (0.84 mmol) of cuprous chloride, 0.175 g (1.27 mmol) of triethylamine hydrochloride, and 3.4 g of acetonitrile. The reaction mixture was heated at reflux for 2 hr and then cooled. Methanol (34 ml) was added to the reaction mixture, and the resulting solution was refrigerated. After standing for 24 hr a white, crystalline solid separated. The solid was filtered, washed with water, and dried to give 14.3 g of crude sulfone. The crude solid was recrystallized from 90% ethanol to give 13.2 g (62% yield) of 3-(benzenesulfonyl)-6-chlorocyclohexene: mp 75–75.5°; nmr (60 MHz, CDCl₃) δ 2.17 (m, 4), 3.80 (m, 1), 4.50 (m, 1), 6.05 (m, 2), and 7.70 (m, 5).

Anal. Calcd for C₁₂H₁₃ClO₂S: C, 56.40; H, 5.11; Cl, 13.80; S, 12.50. Found: C, 56.23; H, 5.09; Cl, 13.51; S, 12.69.

1-(Benzenesulfonyl)-1,3-cyclohexadiene.—To 6.66 g (0.03 mol) of 3-(benzenesulfonyl)-6-chlorocyclohexene in 50 ml of dry benzene was added a solution of 3.52 g (0.035 mol) of triethylamine in 20 ml of dry benzene. The reaction mixture was stirred for 2 hr at room temperature and then filtered to remove the precipitated triethylamine hydrochloride. The benzene was removed *in vacuo* from the resulting filtrate leaving a white solid. The solid was recrystallized from 90% ethanol to give 6.30 g (94% yield) of 1-(benzenesulfonyl)-1,3-cyclohexadiene: mp 92–93°; nmr (60 MHz, CDCl₃) δ 2.32 (s, 4), 6.09 (d, 2), 7.05 (m, 1), and 7.70 (m, 5).

Anal. Calcd for C₁₂H₁₂O₂S: C, 65.45; H, 5.49; S, 14.53. Found: C, 65.22; H, 5.49; S, 14.48.

Reaction of Benzenesulfonyl Chloride with 1,3-Cyclooctadiene. 3-(Benzenesulfonyl)-8-chlorocyclooctene.—In a 100-ml, three-neck flask were placed 10.82 g (0.10 mol) of 1,3-cyclooctadiene,

17.66 g (0.10 mol) of benzenesulfonyl chloride, 0.130 g (1.0 mmol) of cupric chloride, 0.206 g (1.5 mmol) of triethylamine hydrochloride, and 4.0 g of acetonitrile. The reaction mixture was heated, with stirring, at 104° for 2.25 hr and then cooled. Methanol (40 ml) was added to the cooled reaction mixture. The methanol solution was allowed to stand overnight under refrigeration, and a white crystalline solid separated. The solid was filtered, washed with water, dried, and recrystallized from 95% ethanol to give 17.65 g (62% yield) of a mixture of isomers of 3-(benzenesulfonyl)-8-chlorocyclooctene: mp 88–110°; nmr (60 MHz, CDCl₃) δ 1.20–2.50 (m, 8), 4.30–4.85 (m, 2), 5.40–6.15 (m, 2), and 7.25–8.10 (m, 5).

Anal. Calcd for C₁₄H₁₇ClO₂S: C, 59.04; H, 6.02; Cl, 12.45; S, 11.26. Found: C, 59.29; H, 6.18; Cl, 12.48; S, 11.38.

5-Chloro-3-nortricyclyl Phenyl Sulfone.—In a 100-ml three-neck flask were placed 9.21 g (0.10 mol) of bicyclo[2.2.1]hepta-2,5-diene, 17.66 g (0.10 mol) of benzenesulfonyl chloride, 0.130 g (1.0 mmol) of cupric chloride, 0.206 g (1.5 mmol) of triethylamine hydrochloride, and 4.00 g of acetonitrile. The reaction mixture was heated, with stirring, at 90° for 4.5 hr and then cooled. Methanol (40 ml) was added to the cooled reaction mixture, and the resulting solution was refrigerated. After standing under refrigeration overnight, a small amount of a white, crystalline solid separated. The solid was filtered and dried to give 5.40 g (21% yield) of 5-chloro-3-nortricyclyl phenyl sulfone, mp 112.5–113.5°. The sulfone was decolorized and recrystallized from 95% ethanol to give 3.30 g, mp 114–115° (lit.[7] mp 114–116°).

Reaction of Benzenesulfonyl Chloride with Cycloheptatriene. 5-(Benzenesulfonyl)-7-chloro-1,3-cycloheptadiene.—A mixture of 9.20 g (0.10 mol) of cycloheptatriene, 17.66 g (0.10 mol) .of benzenesulfonyl chloride, 0.130 g (1.0 mmol) of cupric chloride, 0.206 g (1.5 mmol) of triethylamine hydrochloride, and 4.00 g of acetonitrile was heated, with stirring, at 120° for 2 hr and then cooled. At the end of the 2 hr reaction period the mixture was a dark, red-brown color. Methanol (40 ml) was added to the cool reaction mixture and a red-brown, crystalline solid separated. The solid was filtered, dried, decolorized, and recrystallized twice from 95% ethanol to give 3.35 g (12.5% yield) of 5-(benzenesulfonyl)-7-chloro-1,3-cycloheptadiene, mp 98–99°. The analytical sample (mp 98–99°) was obtained from another run and was recrystallized twice from hexane, decolorized, and recrystallized twice from 95% ethanol: nmr (60 MHz, CDCl₃) δ 2.00–2.50 (m, 1), 2.60–3.10 (m, 1), 4.15–4.5 (m, 1), 4.80–5.15 (m, 1), 5.95–6.40 (m, 4), and 7.65–8.20 (m, 5).

Anal. Calcd for C₁₃H₁₃ClO₂S: C, 58.10; H, 4.87; Cl, 13.19; S, 11.93. Found: C, 58.00; H, 5.12; Cl, 13.14; S, 11.75.

Reaction of Benzenesulfonyl Chloride with Phenylacetylene.—A mixture of 20.4 g (0.20 mol) of phenylacetylene, 35.30 g (0.20 mol) of benzenesulfonyl chloride, 0.260 g (2.0 mmol) of cupric chloride, 0.412 g (3.5 mmol) of triethylamine hydrochloride, and 8.00 g of acetonitrile was heated, with stirring, at 120° for 2.5 hr and then cooled. Methanol (80 ml) was added to the cooled reaction mixture, a seed crystal of 1-chloro-1-phenyl-2-(benzenesulfonyl)ethene was added, and the solution was refrigerated. After standing under refrigeration overnight, a large amount of yellow-orange solid separated from the methanol solution. The solid was filtered and dried to give 42.25 g of crude sulfone. The crude sulfone was recrystallized twice from hexane to give 24.90 g (45% yield) of 1-chloro-1-phenyl-2-(benzenesulfonyl)ethene, mp 76–78°.

Anal. Calcd for C₁₄H₁₁ClO₂S: C, 60.32; H, 3.98; Cl, 12.72; S, 11.50. Found: C, 60.41; H, 4.14; Cl, 12.66; S, 11.47.

Attempted Reaction of Benzenesulfonyl Chloride with Diphenylacetylene.—A mixture of 8.91 g (0.05 mol) of diphenylacetylene, 8.83 g (0.05 mol) of benzenesulfonyl chloride, 0.065 g (0.5 mmol) of cupric chloride, 0.103 g (0.75 mmol) of triethylamine hydrochloride, and 2.0 g of acetonitrile was heated, with stirring, at 120° for 2 hr and then cooled. Methanol (20 ml) was added to the cooled reaction mixture, and a white, crystalline solid separated. The solid was filtered, washed with water, and dried to give 8.20 (92% recovery) of diphenylacetylene, mp 56–59°.

Registry No.—3, 5829-79-8; 4, 26157-20-0; 6, 26146-14-5; 7, 26146-15-6; 8, 26211-03-0; *cis*-9,

26146-16-7; trans-9, 26146-17-8; 11, 26146-18-9; 12, 26157-21-1.

Notes

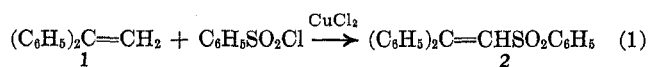## The Copper-Catalyzed Addition of Arenesulfonyl Chlorides to 1,1-Diphenylethylene and Cyclic Aryl-Substituted Olefins[1]

WILLIAM E. TRUCE AND CHRISTIAN T. GORALSKI

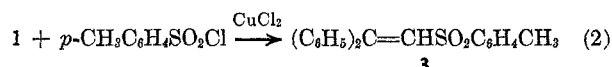*Department of Chemistry, Purdue University, Lafayette, Indiana 47907*

The copper-catalyzed addition of sulfonyl chlorides to simple olefins,[2] conjugated dienes and trienes,[3] and substituted styrenes[4] has been described earlier. In this paper we would like to report our results with 1,1-diphenylethylene and aryl-substituted cyclic olefins.
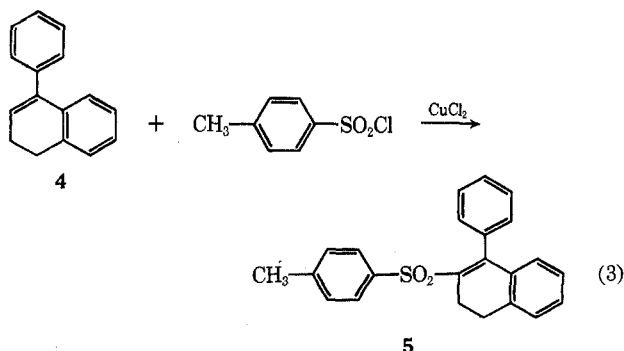
The reaction of benzenesulfonyl chloride and *p*-toluenesulfonyl chloride with 1,1-diphenylethylene (1) gives 1,1-diphenyl-2-(benzenesulfonyl)ethane (2, eq 1) and

$$(C_6H_5)_2C{=}CH_2 + C_6H_5SO_2Cl \xrightarrow{CuCl_2} (C_6H_5)_2C{=}CHSO_2C_6H_5 \quad (1)$$
$$\underset{1}{} \qquad\qquad \underset{2}{}$$

1,1-diphenyl-2-(*p*-toluenesulfonyl)ethene (3, eq 2), re-

$$1 + p\text{-}CH_3C_6H_4SO_2Cl \xrightarrow{CuCl_2} (C_6H_5)_2C{=}CHSO_2C_6H_4CH_3 \quad (2)$$
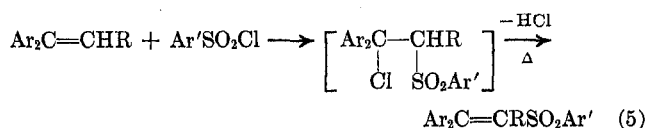$$\underset{3}{}$$

spectively, accompanied by the evolution of hydrogen chloride. A similar reaction was observed with *p*-toluenesulfonyl chloride and 1-phenyl-3,4-dihydronaphthalene (4) to give 1-phenyl-2-(*p*-toluenesulfonyl)-3,4-dihydronaphthalene (5, eq 3).


The reaction does not appear to require two aryl groups on one of the olefinic carbons since 1-phenylcyclohexene (6) reacts with benzenesulfonyl chloride to give 1-phenyl-2-(benzenesulfonyl)cyclohexene (7, eq 4).
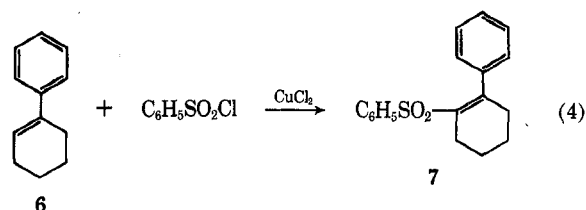
Although this reaction can be regarded as a "direct replacement of a vinyl hydrogen with an arenesulfonyl group," it most certainly involves the intermediacy of a β-chloro sulfone which, under the reaction conditions, spontaneously loses hydrogen chloride to give the observed products (eq 5).

$$Ar_2C{=}CHR + Ar'SO_2Cl \longrightarrow \left[\begin{array}{c} Ar_2C{-}CHR \\ | \quad\ | \\ Cl \ \ SO_2Ar' \end{array}\right] \xrightarrow[\Delta]{-HCl}$$
$$Ar_2C{=}CRSO_2Ar' \quad (5)$$

It has been previously demonstrated with acylic olefins that, when the olefin bears only one aryl substituent, *i.e.*, styrene, the 1:1 adduct with sulfonyl chlorides can be isolated.[2] The same situation apparently holds in the case of cyclic systems, because indene (8) reacts with benzenesulfonyl chloride to afford *trans*-1-chloro-2-(benzenesulfonyl)indan (9, eq 6).
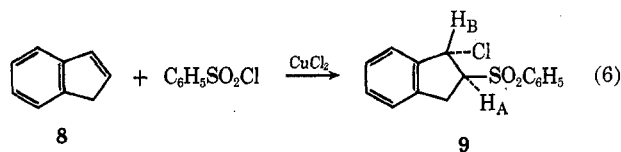
Analysis of the 100-MHz nmr spectrum of 9 indicated that the chlorine and the phenylsulfonyl groups are trans to each other, and that J_{AB} is approximately 4.8–4.9 Hz. The apparent first-order coupling constants for H_A and the adjacent geminal methylene protons are approximately 6.3 and 8.5 Hz.[5] Thus, in the case of indene we have evidence that the copper-catalyzed addition of sulfonyl chlorides to olefins is a trans addition process.

(1) Paper II in the series, Unsaturated Sulfones and Suitable Precursors.
(2) M. Asscher and D. Vofsi, *J. Chem. Soc.*, 4962 (1964).
(3) W. E. Truce, C. T. Goralski, L. W. Christensen, and R. H. Bavry, *J. Org. Chem.*, 35, 4217 (1970).
(4) C. T. Goralski, Ph.D. Thesis, Purdue University, 1969.

(5) We gratefully acknowledge and thank Dr. Thomas E. Evans of the Chemical Physics Research Laboratory, The Dow Chemical Co., Midland, Mich., for determining and interpreting the 100-MHz nmr spectrum.