

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

Acknowledgment.—The authors wish to express

their appreciation for financial support of this work by the Purdue Research Foundation and the Public Health Service Research Grant No. CA-04536-11 from the National Cancer Institute.

Notes

The Copper-Catalyzed Addition of Arenesulfonyl Chlorides to 1,1-Diphenylethylene and Cyclic Aryl-Substituted Olefins¹

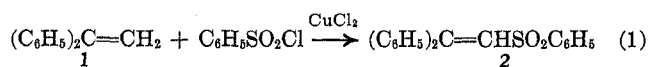
WILLIAM E. TRUCE AND CHRISTIAN T. GORALSKI

Department of Chemistry, Purdue University,
Lafayette, Indiana 47907

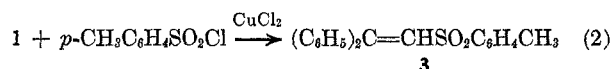
Received May 22, 1970

The copper-catalyzed addition of sulfonyl chlorides to simple olefins,² conjugated dienes and trienes,³ and substituted styrenes⁴ has been described earlier. In this paper we would like to report our results with 1,1-diphenylethylene and aryl-substituted cyclic olefins.

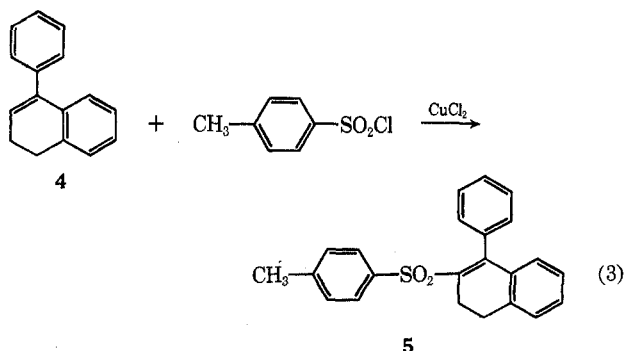
The reaction of benzenesulfonyl chloride and *p*-toluenesulfonyl chloride with 1,1-diphenylethylene (1) gives 1,1-diphenyl-2-(benzenesulfonyl)ethane (2, eq 1) and



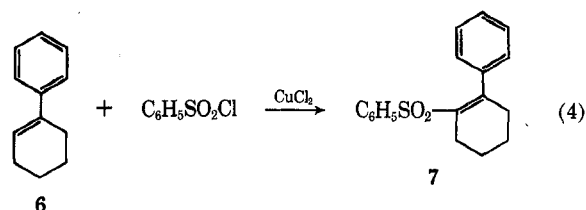
1,1-diphenyl-2-(*p*-toluenesulfonyl)ethane (3, eq 2), re-



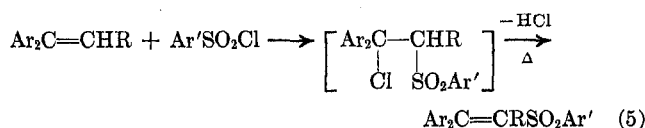
spectively, accompanied by the evolution of hydrogen chloride. A similar reaction was observed with *p*-toluenesulfonyl chloride and 1-phenyl-3,4-dihydronaphthalene (4) to give 1-phenyl-2-(*p*-toluenesulfonyl)-3,4-dihydronaphthalene (5, eq 3).



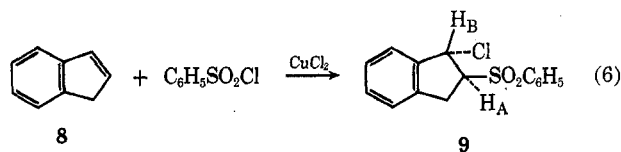
The reaction does not appear to require two aryl groups on one of the olefinic carbons since 1-phenylcyclohexene (6) reacts with benzenesulfonyl chloride to give 1-phenyl-2-(benzenesulfonyl)cyclohexene (7, eq 4).



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).



It has been previously demonstrated with acyclic 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).

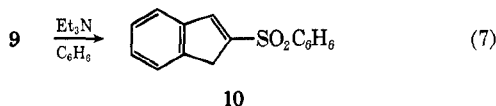


Analysis of the 100-MHz nmr spectrum of 9 indicated that the chlorine and the phenylsulfonyl groups are *trans* to each other, and that J_{AB} is approximately 4.8–4.9 Hz. The apparent first-order coupling constants for H_A and the adjacent geminal methylene protons are approximately 6.3 and 8.5 Hz.⁵ Thus, in the case of indene we have evidence that the copper-catalyzed addition of sulfonyl chlorides to olefins is a *trans* addition process.

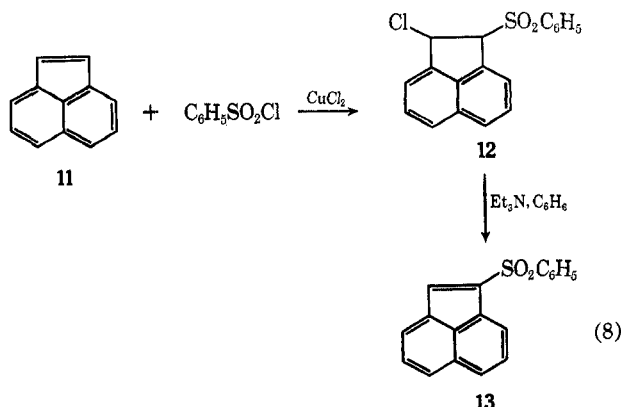
(1) Paper II in the series, *Unsaturated Sulfones and Suitable Precursors*.
 (2) M. Asscher and D. Vofsi, *J. Chem. Soc.*, 4962 (1964).
 (3) W. E. Truce, C. T. Goralski, L. W. Christensen, and R. H. Bavry, *J. Org. Chem.*, **35**, 4217 (1970).
 (4) C. T. Goralski, Ph.D. Thesis, Purdue University, 1969.

(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.

Treatment of **9** with triethylamine in benzene afforded 2-(benzenesulfonyl)indene (**10**) in excellent yield (eq 7).



The reaction of benzenesulfonyl chloride with acenaphthalene (**11**) behaved differently in that the β -chloro sulfone (**12**) could not be isolated; treatment of the crude reaction mixture with triethylamine in benzene gave 1-(benzenesulfonyl)acenaphthalene (**13**, eq 8).



In conclusion, the copper-catalyzed addition of sulfonyl chlorides to aryl-substituted cyclic olefins constitutes one- and two-step synthetic routes to α,β -unsaturated sulfones which previously had been difficult to prepare.

Experimental Section^{6,7}

1,1-Diphenyl-2-(benzenesulfonyl)ethene.—A mixture of 9.00 g (0.05 mol) of 1,1-diphenylethylene, 8.83 g (0.05 mol) of benzenesulfonyl chloride, 0.065 g (0.50 mmol) of anhydrous cupric chloride, 0.103 g (0.75 mmol) of triethylamine hydrochloride, and 2.0 g of acetonitrile was heated, with stirring, at 135° for 2 hr and then cooled. Methanol (20 ml) was added to the cooled reaction mixture and the sulfone separated as a pale yellow, crystalline solid. The sulfone was recrystallized from 95% ethanol, once from benzene, and again from 95% ethanol to give 9.41 g (59% yield) of 1,1-diphenyl-2-(benzenesulfonyl)ethene, mp 114–115°.

Anal. Calcd for $\text{C}_{20}\text{H}_{16}\text{O}_2\text{S}$: C, 74.97; H, 5.03; S, 10.01. Found: C, 75.10; H, 4.98; S, 9.80.

1,1-Diphenyl-2-(*p*-toluenesulfonyl)ethene.—A mixture of 9.0 g (0.05 mol) of 1,1-diphenylethylene, 9.5 g (0.05 mol) of *p*-toluenesulfonyl chloride, 0.065 g (0.50 mmol) of anhydrous cupric chloride, 0.103 g (0.75 mmol) of triethylamine hydrochloride, and 2.0 g of acetonitrile was heated, with stirring, at 130° for 2 hr and then cooled. Hydrogen chloride gas was evolved during the entire 2-hr reaction period. Methanol (20 ml) was added to the cooled reaction mixture and the sulfone separated as a white, crystalline solid. The crude sulfone was filtered, dried, and recrystallized from 95% ethanol to give 8.0

(6) All reactions were carried out in a nitrogen atmosphere. Reagent grade cupric chloride was used in all addition reactions, and it was dried at 140° prior to use. The 60-MHz nmr spectra were recorded on a Varian A-60 spectrometer with tetramethylsilane as an internal standard (TMS = 0). The 100-MHz nmr spectra were recorded on a Varian HA-100 spectrometer locked on tetramethylsilane as a reference signal (see ref 5). All melting points are uncorrected. The elemental analyses were performed by Dr. C. S. Yeh and the staff of the Purdue Microanalytical Laboratory.

(7) 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).

g (48% yield) of 1,1-diphenyl-2-(*p*-toluenesulfonyl)ethene, mp 104–105.5° (lit.⁸ mp 103–104°).

Anal. Calcd for $\text{C}_{21}\text{H}_{18}\text{O}_2\text{S}$: C, 75.42; H, 5.42; S, 9.59. Found: C, 75.40; H, 5.43; S, 9.56.

1-Phenyl-2-(*p*-toluenesulfonyl)-3,4-dihydronaphthalene.—A mixture of 10.30 g (0.05 mol) of 1-phenyl-3,4-dihydronaphthalene, 9.53 g (0.05 mol) of *p*-toluenesulfonyl chloride, 0.065 g (0.50 mmol) of anhydrous cupric chloride, 0.103 g (0.75 mmol) of triethylamine hydrochloride, and 2.0 g of acetonitrile was heated, with stirring, at 130° for 2 hr and then cooled. Hydrogen chloride gas was evolved during the entire 2-hr reaction period. Ethanol (20 ml) was added to the cooled reaction mixture and the sulfone separated as a white crystalline solid. The solid was filtered, dried, and recrystallized from 95% ethanol to give 8.05 g (45% yield) of 1-phenyl-2-(*p*-toluenesulfonyl)-3,4-dihydronaphthalene, mp 160.5–162°. The sulfone was recrystallized once again from 95% ethanol and once from benzene-hexane to give 6.10 g: mp 163.5–164.5°; nmr (60 MHz, CDCl_3) δ 2.38 (s, 3); 2.97 (s, 4), 6.60–7.70 (mult, 13).

Anal. Calcd for $\text{C}_{23}\text{H}_{20}\text{O}_2\text{S}$: C, 76.63; H, 5.59; S, 8.90. Found: C, 76.91; H, 5.65; S, 8.76.

***trans*-1-Chloro-2-(benzenesulfonyl)indan.**—A mixture of 11.62 g (0.10 mol) of indene, 17.66 g (0.10 mol) of benzenesulfonyl chloride, 0.130 g (1.0 mmol) of anhydrous cupric chloride, 0.206 g (1.5 mmol) of triethylamine hydrochloride, and 4.0 g of acetonitrile was heated, with stirring, at 116° for 2 hr and then cooled. Methanol (40 ml) was added to the cooled reaction mixture and the crude sulfone separated as a tan solid. The solid was filtered, dried, decolorized, and recrystallized from 95% ethanol to give 11.90 g (41% yield) of *trans*-1-chloro-2-(benzenesulfonyl)indan: mp 82–83°; nmr (100 MHz, CDCl_3) δ 3.46 (3 lines, 2), 4.16 (8 lines, 1), 5.71 (d, 1), 7.02–8.00 (3 mult, 9).

Anal. Calcd for $\text{C}_{15}\text{H}_{13}\text{ClO}_2\text{S}$: C, 61.53; H, 4.47; Cl, 12.11; S, 10.95. Found: C, 61.18; H, 4.60; Cl, 12.12; S, 10.97.

2-(Benzenesulfonyl)indene.—To 8.76 g (0.03 mol) of *trans*-1-chloro-2-(benzenesulfonyl)indan in dry benzene was added 4.54 g (0.045 mol) of triethylamine. The reaction mixture was stirred for 2 hr at room temperature and was then filtered to remove the triethylamine hydrochloride which had separated. The triethylamine hydrochloride was washed with several portions of dry benzene. The benzene was removed *in vacuo* from the combined benzene filtrates leaving a yellow oil which crystallized on addition of a small amount of 95% ethanol. The solid was filtered and dried to give 4.1 g (53% yield) of 2-(benzenesulfonyl)indene, mp 120–122°. The sulfone was recrystallized from 95% ethanol to give 3.5 g: mp 121–122°; nmr (60 MHz, CDCl_3) δ 3.63 (d, 2), 7.20–7.80 (mult, 8), 7.90–8.25 (mult, 2).

Anal. Calcd for $\text{C}_{15}\text{H}_{12}\text{O}_2\text{S}$: C, 70.28; H, 4.72; S, 12.51. Found: C, 70.08; H, 4.65; S, 12.54.

1-(Benzenesulfonyl)acenaphthalene.—A mixture of 15.22 g (0.10 mol) of acenaphthalene, 17.67 g (0.10 mol) of benzenesulfonyl chloride, 0.130 g (1.0 mmol) of anhydrous cupric chloride, 0.206 g (1.5 mmol) of triethylamine hydrochloride, and 4.0 g of acetonitrile was heated, with stirring, at 100° for 2 hr and then cooled. The cooled reaction mixture was a dark brown, semisolid mass. The cooled reaction mixture was dissolved in benzene and 1 equiv of triethylamine was added. The benzene solution was filtered to remove the triethylamine hydrochloride which had separated. The triethylamine hydrochloride was washed with several portions of dry benzene. The combined benzene filtrates were cooled and the crude sulfone separated as an orange, crystalline solid. The crude sulfone was recrystallized from 95% ethanol to give 14.40 g (49% yield) of 1-(benzenesulfonyl)acenaphthalene as bright yellow crystals, mp 133–133.5°.

Anal. Calcd for $\text{C}_{18}\text{H}_{12}\text{O}_2\text{S}$: C, 73.97; H, 4.14; S, 10.97. Found: C, 74.13; H, 4.17; S, 11.09.

Registry No.—1,1-Diphenylethylene, 530-48-3; 1,1-diphenyl-2-(benzenesulfonyl)ethene, 26189-62-8; 1-phenyl-2-(*p*-toluenesulfonyl)-3,4-dihydronaphthalene, 26189-63-9; *trans*-1-chloro-2-(benzenesulfonyl)indan, 26189-64-0; 2-(benzenesulfonyl)indene, 26189-65-1; 1-(benzenesulfonyl)acenaphthalene, 26159-62-6.

(8) C. M. M. da Silva Correa and W. A. Waters, *J. Chem. Soc. C*, 1874 (1968).

Acknowledgment.—The authors wish to express their appreciation for financial support of this work by the Purdue Research Foundation and the Public Health Service Research Grant No. CA-04536-11 from the National Cancer Institute.

The [2 + 2] Photocycloadditions of Indene and 2- and 3-Chloroindenes

G. W. GRIFFIN* AND U. HEEP

Department of Chemistry,
Louisiana State University in New Orleans,
Lake Front, New Orleans, Louisiana 70122

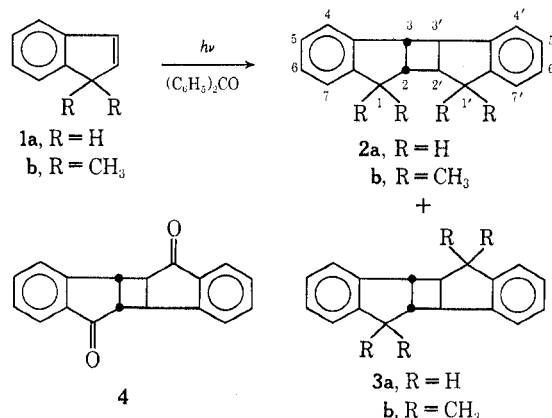
Received May 14, 1970

As a consequence of our continuing interest in the mechanism and stereochemistry of [2 + 2] photocycloadditions¹ and in the introduction of multiple trigonal centers into the resulting cyclobutyl products we have extended our previous studies of indenenes² to haloindene derivatives. It was anticipated that dimers and crossed cycloadducts of the latter substrates might be dehydrohalogenated or dehalogenated to unsaturated systems of potential theoretical interest. The photosensitized dimerization of indene **1a** was first reported by Schenck,³ and the primary product (mp 110–112°) was shown in our laboratories to have the truxane structure **2a** with syn (head-to-head), trans stereochemistry by degradative ozonolysis to *cis,trans,cis*-tetracarboxycyclobutane and conversion to a truxone (in the formal sense an indenone dimer) of syn orientation.^{2a-c} The same conclusion was reached independently by Bowyer and Porter by stereospecific oxidative conversion of the indene photodimer to the coumarin dimer of known syn, trans stereochemistry.⁴

Recently, McCullough has studied the direct and photosensitized dimerization of 1,1-dimethylindene (**1b**) and found that two dimers, the syn, trans and anti, trans isomers, **2b** and **3b**, respectively, are formed in a 5:1 ratio when acetophenone is employed as a photosensitizer.⁵ The structures of the two dimers were assigned on the basis of nmr spectroscopy and it is noteworthy that the major product **2b** has syn, trans stereochemistry which is consistent with the results obtained with indene.

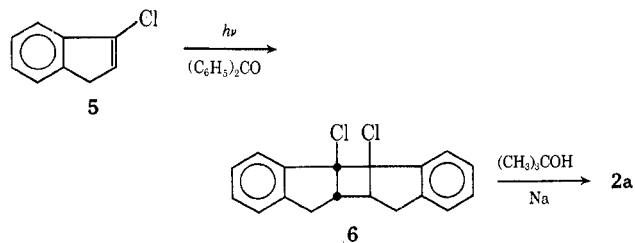
During a recent attempt to recover additional **2a** from the combined residues obtained from several irradiations

of indene by elution chromatography on silica gel, a previously unreported photodimer was isolated in low yield having a melting point of 142–143° consistent with



that reported for α -truxane, the anti, trans isomer **3a**.⁴ Upon oxidation of **3a** with sodium dichromate in glacial acetic acid, according to previously described techniques,⁴ a truxone was obtained with mp 296–297° in agreement with the melting point reported for **4** obtained by cyclization of α -truxillic acid.^{6,7}

When 3-chloroindene (**5**)⁸ is irradiated in benzene with benzophenone as a sensitizer a photodimer **6** is obtained (20–30%) which upon recrystallization from cyclohexane deposits in two crystal modifications (mp 169–170° and 179–180°). That the stereochemistry of **6**, the major dimeric product, is syn, trans was established by reductive dehalogenation with sodium in tetrahydrofuran containing *tert*-butyl alcohol which



gave exclusively **2a** in high yield.⁹ The nmr spectrum of **6** (deuteriochloroform, 60 MHz) exhibits signals for the aromatic protons at τ 2.20 and 2.65 and multiplets for the remaining protons at τ 6.40–7.60. Clearly the preferred mode of dimerization observed for **5** is consistent with that found for **1a** and **1b**.

The crossed cycloaddition of indene to 2-chloroindene (**7**) was accomplished by Krauch and Metzner. While a syn orientation may be inferred for the adduct from the thermolysis product, namely 2,2'-biindenyl, a complete structural assignment was not reported.¹⁰ We have investigated the benzophenone sensitized crossed cycloaddition of indene to 3-chloroindene (**5**). 3,3'-Dichlorotruxane (**6**) and small amounts of *syn,trans*-

* To whom correspondence should be addressed.

(1) L. Due, R. A. Mateer, L. Brassier, and G. W. Griffin, *Tetrahedron Lett.*, 6173 (1968).

(2) A. G. Anastassiou, Ph.D. Thesis, Yale University, 1963; (b) A. G. Anastassiou, F. L. Setliff, and G. W. Griffin, *J. Org. Chem.*, **31**, 2705 (1966); (c) A. G. Anastassiou and G. W. Griffin, *ibid.*, **33**, 3441 (1968); (d) F. L. Setliff, A. G. Anastassiou, and G. W. Griffin, *ibid.*, **34**, 3047 (1969); (e) G. W. Griffin, A. F. Marcantonio, H. Kristinsson, R. C. Petterson, and C. S. Irving, *Tetrahedron Lett.*, 2951 (1965).

(3) G. O. Schenck, W. Hartmann, S. P. Mannsfeld, W. Metzner, and C. H. Krauch, *Chem. Ber.*, **95**, 1642 (1962). C. H. Krauch, W. Metzner, and G. O. Schenck, *Naturwissenschaften*, **50**, 710 (1963); Belgium Patent 630,110 (1963); *Chem. Abstr.*, **60**, 15801 (1964).

(4) J. Bowyer and Q. N. Porter, *Aust. J. Chem.*, **19**, 1455 (1966); *Chem. Abstr.*, **65**, 13643 (1966).

(5) (a) J. J. McCullough, *Can. J. Chem.*, **46**, 43 (1958). (b) A dimer of unknown structure was also obtained upon irradiation of 1,1-diphenylindene; however, it was shown to arise from the product of a rearrangement of the type we had reported earlier for 1,3,3-triphenylindene^{2a} and not from 1,1-diphenylindene.^{5a}

(6) (a) R. Stoermer and G. Foerster, *Chem. Ber.*, **52**, 1255 (1919); (b) E. H. White and H. C. Dunathan, *J. Amer. Chem. Soc.*, **78**, 6055 (1956).

(7) Metzner and Wendisch have shown that the direct and photosensitized dimerization of indene gives **2a** (83%) and **3a** (9%) in addition to lower yields of the other possible isomeric truxanes, namely the *syn,cis* and *anti,cis* modifications (3 and 5%, respectively). See W. Metzner and D. Wendisch, *Justus Liebig's Ann. Chem.*, **730**, 111 (1969).

(8) E. A. Braude and L. A. Evans, *J. Chem. Soc.*, 3337 (1955).

(9) P. G. Gassman, D. H. Aue, and D. S. Patton, *J. Amer. Chem. Soc.*, **90**, 7271 (1968).

(10) C. H. Krauch and W. Metzner, *Chem. Ber.*, **98**, 2762 (1965).