4-Acetylthiophenol (1 g.) and 2 g. of mercuric oxide in 20 cc. of dry pyridine was heated 10 min. on a steam-bath; excess mercuric oxide was filtered off, and upon addition of water and chilling, 1.5 g. of buff flakes was obtained which, after recrystallizing from nitrobenzene, melted at 225–227°.

Anal. Calcd. for $C_{16}H_{14}O_2S_2Hg$: C, 38.20; H, 2.80. Found: C, 38.24; H, 3.05.

This mercuric mercaptide turns yellow upon heating and is readily soluble in cold pyridine.

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1,2-Bis-(arylsulfonyl)-ethenes in the Diels–Alder Reaction

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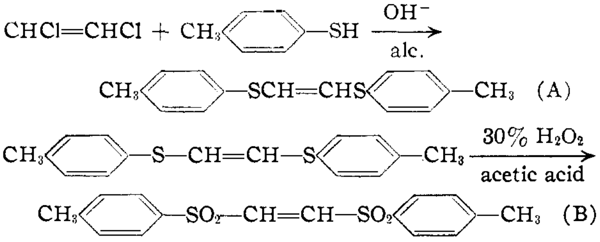
The preparation and Diels–Alder reactions of 1,2-bis-(phenylsulfonyl)-ethene and 1,2-bis-(*p*-tolylsulfonyl)-ethene are described. The compounds mentioned are presumably the *trans* isomers. They are reactive dienophiles toward cyclopentadiene, isoprene, butadiene and anthracene. No reaction with furan was observed.

The recent work of Snyder and Hallada,[1] dealing with the use of α,β-unsaturated sulfonyl compounds in the Diels–Alder reaction, has made presentation of our related work desirable. It has been possible to isolate both the *cis* and the *trans* isomers of bis-(*p*-tolylsulfonyl)-ethene, whereas the above authors worked with only one isomer. While the present work with the low melting form, which is, presumably, the *cis* compound,[2] is a duplication of their results and is not discussed further, the series of Diels–Alder adducts obtained from the "*trans*" form are new.

The original intention was to prepare a series of adducts with 1,2-bis-(phenylsulfonyl)-ethene, but poor yields of the intermediate 1,2-bis-(phenylmercapto)-ethene led to the use of 1,2-bis-(*p*-tolylsulfonyl)-ethene. However, the 1,2-bis-(phenylsulfonyl)-ethene isolated in the preliminary work was a high melting solid (229°). This fact led to the expectation that a high melting isomer of 1,2-bis-(*p*-tolylsulfonyl)-ethene should also exist. Previous authors[1,3] obtained only the low melting isomer by the reactions



Substitution of a longer reaction time in step A and use of glacial acetic acid in step B gave a mixture of disulfones which could be separated by their solubility differences.

The 1,2-bis-(arylsulfonyl)-ethenes were found to be highly reactive dienophiles in reactions with cyclopentadiene, isoprene, butadiene and anthracene. The reaction with furan does not occur in ether at room temperature, in refluxing benzene, or in benzene at 115°. The reaction with anthracene is of interest. Snyder and Hallada[1] report the isolation of two isomeric adducts of "*cis*" bis-(*p*-tolylsulfonyl)-ethene and anthracene, which were believed to be *meso* and racemic forms. In the present work, the "*trans*" bis-(*p*-tolylsulfonyl)-ethene gave only the lower melting compound, presumably the racemic mixture. In the previous work,[1] partial isomerization of the low melting bis-(*p*-tolylsulfonyl)-ethene by the heat necessary to secure reaction with anthracene evidently occurred, resulting in the two isomers obtained. This isomerization of the low melting compound lends further credence to the assignment of the *cis* structure to it, since the *cis* isomer is usually the labile form.[4]

The decomposition of butadiene sulfone in dibutyl ether to give butadiene usable in a Diels–Alder reaction constitutes an improvement, in our opinion, over the usual closed tube method of carrying out such reactions with butadiene, at least in the cases reported here.

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Experimental

1,2-Bis-(phenylsulfonyl)-ethene.—1,2-Bis-(phenylmercapto)-ethene (2.4 g., 0.01 mole), which had been prepared by the method of Cusa and McCombie,[5] was dissolved in 100 ml. of glacial acetic acid and the resulting solution heated to reflux temperature. Ten grams of 30% hydrogen peroxide was added and the refluxing continued for 2.5 hours. Refrigeration and filtration gave 1.1 g. of crystalline solid melting at 228°. Trituration with 95% alcohol gave 1.0 g. (32%) of solid melting at 229°.

Anal. Calcd. for $C_{14}H_{12}O_4S_2$: C, 54.52; H, 3.93. Found: C, 54.39; H, 4.01.

Reduction of this compound with zinc and glacial acetic acid gave the known 1,2-bis-(phenylsulfonyl)-ethane.[6]

1,2-Bis-(*p*-tolylmercapto)-ethene.—The method of Fromm and Seibert[3] was modified in this preparation. *p*-Toluenethiol (124.2 g., 1.0 mole) was added to 1440 ml. of 7% alcoholic potassium hydroxide in a three-neck flask equipped with stirrer, reflux condenser and addition funnel. The solution was heated to reflux, then *cis*-dichloroethylene (50 g., 0.52 mole) in 100 ml. of ethanol was added dropwise over a period of seventeen hours. After addition was complete, reflux was continued for two hours. The solution was filtered while hot. The salt residue was extracted twice with 100-ml. portions of boiling ethanol, and these extracts added to the filtrate. On cooling, 133 g. of crude solid, m.p. 83–90°, was obtained (97.8%). Recrystallization from

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[1] H. R. Snyder and D. P. Hallada, THIS JOURNAL, **74**, 5595 (1952).

[2] H. Gilman, "Organic Chemistry," Vol. I, Second Edition, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 450.

[3] E. Fromm and B. Seibert, *Ber.*, **55**, 1014 (1922).

[4] Reference 2, p. 453.

[5] N. W. Cusa and H. McCombie, *J. Chem. Soc.*, 767 (1937).

[6] R. Otto, *Ber.*, **13**, 1280 (1880).

95% alcohol yielded 119.4 g. (88%) of 1,2-bis-(*p*-tolylmercapto)-ethene, m.p. 90–91° (lit.[3] 93°).

1,2-Bis-(*p*-tolylsulfonyl)-ethenes.—1,2-Bis-(*p*-tolylmercapto)-ethene (68.1 g., 0.25 mole) was dissolved in 300 ml. of refluxing glacial acetic acid, then 226 g. (*ca.* 4.0 moles) of 30% hydrogen peroxide was added rapidly. After addition was complete, reflux was continued for two hours. On cooling, 61 g. of crude disulfone, m.p. 147–153°, was obtained. An additional 5.3 g., m.p. 143–145°, was obtained by recrystallization from alcohol (95%) of the product obtained by evaporating the mother liquor to one-half volume and adding an equal volume of water. Recrystallization of combined crops from hot 95% alcohol gave 31.1 g. (37%) of the soluble expected disulfone, m.p. 149° (lit.[3] 149–150°), and 26.2 g. (31%) of its slightly soluble geometrical isomer, m.p. 228–229°.

Anal. Calcd. for $C_{16}H_{16}O_4S_2$: C, 57.12; H, 4.71. Found: C, 56.89; H, 4.60.

Reduction of Isomeric 1,2-Bis-(*p*-tolylsulfonyl)-ethenes.—Four grams of the isomer melting at 228–229° was dissolved in 150 ml. of boiling glacial acetic acid; 7 g. of zinc dust was added in small portions over a period of one hour. Reflux was continued one-half hour longer, after which the mixture was filtered while hot. On standing at room temperature 2.34 g. (58%) of tiny white needles, m.p. 204–205°, was obtained. A mixed melting point with an authentic sample[7] of 1,2-bis-(*p*-tolylsulfonyl)-ethane showed no depression.

3,6-Methano-4,5-bis-(phenylsulfonyl)-cyclohexene.—A mixture (1.6 g., 0.024 mole) of freshly distilled cyclopentadiene, 3.7 g., 0.012 mole, of 1,2-bis-(phenylsulfonyl)-ethene (m.p. 228–229°), and 100 ml. of benzene were refluxed for 17 hours. After chilling, 2.9 g. of solid melting 169.5–171.5° was obtained. Washing of the residue left by evaporation of the filtrate with boiling 30–60° petroleum ether left 1.3 g. of solid, m.p. 164–167°; crude yield 4.2 g. (93%). Recrystallization from benzene–ethanol (1:1) gave 3.8 g. (84%) of solid melting 169–170°.

Anal. Calcd. for $C_{19}H_{18}O_4S_2$: C, 60.94; H, 4.84. Found: C, 60.74; H, 4.89.

Dibromide: m.p. 216°. *Anal.* Calcd. for $C_{19}H_{18}O_4Br_2S_2$: Br, 29.91. Found: Br, 30.04.

4,5-Bis-(phenylsulfonyl)-cyclohexene.—1,2-Bis-(phenylsulfonyl)-ethene (0.924 g., 0.003 mole), butadiene sulfone (1.062 g., 0.009 mole) and 100 ml. of dry dibutyl ether were placed in a 200-ml. three-neck flask equipped with stirrer, thermometer and condenser. The temperature was raised to 122° and maintained there, with stirring, for 13 hours. Refrigeration produced 1.015 g. of crude adduct (93%), m.p. 162–163°. Recrystallization from hot ethanol to which water was added until solution became cloudy gave 0.82 g. (75%) of product melting at 167.5–168°.

Anal. Calcd. for $C_{18}H_{18}O_4S_2$: C, 59.64; H, 5.00. Found: C, 59.76; H, 5.01.

4,5-Bis-(*p*-tolylsulfonyl)-cyclohexene.—Bis-(*p*-tolylsulfonyl)-ethene, m.p. 228–229° (6.728 g., 0.02 mole), and butadiene sulfone (4.728 g., 0.04 mole) were placed in 180 ml. of dibutyl ether and the mixture heated at 115° for 23 hours. The solution was filtered while hot. The residue was extracted with 50 ml. of hot alcohol, filtered and chilled. Two crops from the dibutyl ether and one from the alcohol gave 7.059 g., 90.4% of crude product. Decolorization with norite and recrystallization from alcohol gave 5.180 g. (68%), of solid melting 168–174°.

Anal. Calcd. for $C_{20}H_{22}O_4S_2$: C, 61.51; H, 5.68. Found: C, 61.24; H, 5.80.

3,6-Methano-4,5-bis-(*p*-tolylsulfonyl)-cyclohexene.—Bis-(*p*-toluenesulfonyl)-ethene, m.p. 228–229° (5.00 g., 0.015 mole), was added to 150 ml. of benzene and the solution refluxed. The solid did not dissolve. Addition of 7 ml. of freshly distilled cyclopentadiene resulted in dissolution of the solid in 2–3 minutes. (This behavior is in contradistinction with that of the 149° isomer, which is itself soluble, but produces an insoluble adduct.) After refluxing for one-half hour the solution was chilled overnight in a refrigerator. Only a small amount of solid had formed. The solvent was removed under an air jet leaving a white residue, which melted 150–158°. Recrystallization from ethanol–benzene (2:1) gave, in two crops, 5.31 g. (89.2%) of solid, m.p. 158–161°. A further recrystallization of a portion from methanol–benzene (2:1) gave a solid melting 162–163°.

Anal. Calcd. for $C_{21}H_{22}O_4S_2$: C, 62.66; H, 5.51. Found: C, 62.66; H, 5.93.

1-Methyl-4,5-bis-(*p*-tolylsulfonyl)-cyclohexene.—1,2-Bis-(*p*-tolylsulfonyl)-ethene, m.p. 228–229° (0.40 g., 0.0012 mole) was dissolved in a mixture of 10 ml. of benzene and 3 ml. of isoprene. The resulting mixture was refluxed 48 hours. The solution was then evaporated to dryness under an air jet. A tan residue weighing 0.62 g. and melting 140–149° was obtained. Recrystallization from 95% alcohol gave 0.37 g. (77%) of solid melting at 151–152°.

Anal. Calcd. for $C_{21}H_{24}O_4S_2$: C, 62.47; H, 5.95. Found: C, 62.44; H, 5.84.

Adduct of Anthracene and "trans" Bis-(*p*-(tolylsulfonyl)-ethene.—This preparation follows that of Snyder and Hallada[1] with the exception that the high melting isomer of 1,2-bis-(*p*-tolylsulfonyl)-ethene was used. A mixture of 0.50 g. (0.0015 mole) of 1,2-bis-(*p*-tolylsulfonyl)-ethene, m.p. 228–229°, and 0.265 g. (0.0015 mole) of anthracene, were fused in a test-tube, then heated by immersion of the test-tube in refluxing bromobenzene for 20 hours. The solid that formed on cooling was boiled with 50 ml. of ethanol. After cooling, the mixture was filtered and yielded 0.63 g. (82%) of ethanol insoluble adduct. Trituration with hot ethanol and recrystallization from acetone–water (9:1) gave a solid melting 239–241° (lit.[1] 239.5–241°). No material corresponding to the other isomer reported by Snyder and Hallada[1] could be found.

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(7) E. Fromm and E. Seibert, *Ber.*, **55**, 1029 (1922).