components, of the known and unknown mixtures were again taken, and the compositions of the known and unknown mixtures calculated by solving two sets of three simultaneous equations in three unknowns. The two equations based on the optical densities at λ = 11.98 and 12.16 μ were used in each set of solutions, the optical densities at 9.97 μ being used in one set of solutions and at 10.88 μ in the other. The compositions of the unknown mixtures were then corrected to those of the known mixtures for deviations from Beer's law. The pertinent data are set forth in Table III.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Stereoisomeric 1,2-Bis-(arylmercapto)-ethenes and Corresponding Sulfones[1]

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The stereoisomeric 1,2-bis-(phenylmercapto)-ethenes and 1,2-bis-(*p*-tolylmercapto)-ethenes were prepared and related to the corresponding *cis*- and *trans*-sulfones by a mild non-isomerizing oxidation. In the phenyl series, assignment of *cis* and *trans* structures on the basis of the isomers' solubilities and melting points is consistent for the sulfides and sulfones. However, in the *p*-tolyl series the sulfides exhibit anomalous melting point and solubility behavior, in that the low melting, more soluble isomer is related structurally to the high melting, more insoluble sulfone. Infrared spectra and dipole moments of the 1,2-bis-(*p*-tolylmercapto)-ethenes and 1,2-bis-(*p*-tolylsulfonyl)-ethenes, respectively, confirm the empirical assignments of structure.

In an earlier paper[2] the geometrical isomers of 1,2-bis-(*p*-tolylsulfonyl)-ethene were assigned *cis* and *trans* structures by the empirical criteria that a *trans* isomer is usually the higher melting, more insoluble and less thermally-labile form.[3] Both isomers were prepared by the action, at reflux temperature, of 30% hydrogen peroxide and glacial acetic acid on the single known[4] 1,2-bis-(*p*-tolylmercapto)-ethene. In the present work the isomeric 1,2-bis-(*p*-tolylmercapto)-ethene was prepared by a partial thermal isomerization of the known isomer, and both compounds were oxidized under conditions such that each sulfide was related structurally to one of the isomeric 1,2-bis-(*p*-tolylsulfonyl)-ethenes (Fig. 1). It will be noted that the low melting (and more soluble) sulfide II is related structurally to the high melting (and more insoluble) sulfone IV. These results cast some doubt on the empirical assignments of *cis* and *trans* structures to the sulfones, for assignment of structures to the sulfides on the same basis would result in a "*cis*" sulfide being related geometrically to a "*trans*" sulfone. However, with the 1,2-bis-(phenylmercapto)-ethenes and the corresponding sulfones (Fig. 1), a regular relationship exists in that the higher melting and more insoluble sulfide VI is related to the more insoluble and higher melting sulfone VIII.

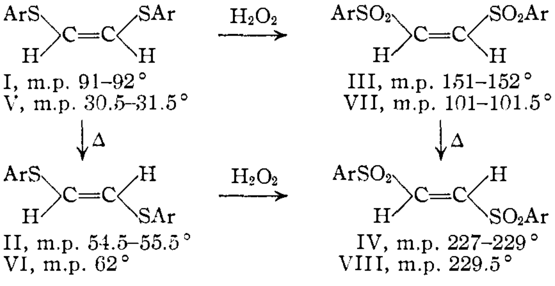

Fig. 1.—Relationships among the 1,2-bis-(arylmercapto)-ethenes and the corresponding sulfones. Ar is *p*-tolyl for I, II, III, IV and phenyl for V, VI, VII, VIII.

Conclusive confirmation of the original structure assignments for *cis*- and *trans*-1,2-bis-(*p*-tolysulfonyl)-ethenes and the corresponding sulfides are the dipole moments and infrared spectra, respectively, of these compounds. The lower melting sulfone has the higher dipole moment, indicative of a *cis* configuration. Furthermore, the lower melting sulfide (corresponding to the higher melting sulfone) has an absorption band at 10.88 μ. Although the *trans*-double bond absorption occurs in straight chain olefins at 10.36 μ, this shift (0.5 μ) is not infrequent when certain polar groups are held by the double bond.[5]

Chemical methods of verifying the assignments of the *cis* and *trans* structures shown in Fig. 1 were attempted. Although the results were inconclusive, they are of some interest. Since the elimination of hydrogen chloride occurs much more readily from *cis*-dichloroethylene than from *trans*-dichloroethylene,[6] it was thought that a similar difference might exist for the reaction of the 1,2-bis-(*p*-tolysulfonyl)-ethenes with base. It had been reported that the 1,2-bis-(*p*-tolysulfonyl)-ethene melting at 149–150° was stable to base,[4] which indicated that the low melting, more soluble isomer might be the *trans* form. However, both isomers react with base; the low melting isomer appears to react faster. But this result is not necessarily consistent with the empirical assignment of configuration, since the initial step in the reaction was probably a nucleophilic addition to the olefinic bond, and since the poor solubility of the sulfones resulted in heterogeneous reaction mixtures. To obviate the first of these complications, the adducts of the 1,2-bis-(*p*-tolylsulfonyl)-ethenes with cyclopentadiene were considered. Since the Diels–Alder reaction proceeds by a "*cis*" addition, the arrangements in space of the sulfonyl groups should be essentially retained in the adducts. If the original structure assignments

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[1] Presented at the Kansas City Meeting of the American Chemical Society, March 24, 1954.

[2] W. E. Truce and R. J. McManimie, THIS JOURNAL, **75**, 1672 (1953).

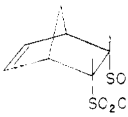
[3] (a) H. Gilman, "Organic Chemistry," Vol. I, 2nd Edition, John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 449–453; (b) L. Crombie, *Quarterly Revs.*, **6**, 101 (1952).

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

[5] J. D. Stroupe, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March, 1952.

[6] S. I. Miller and R. M. Noyes, THIS JOURNAL, **74**, 629 (1952).

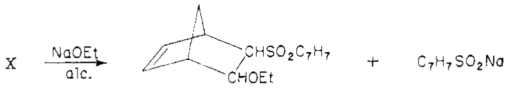
were correct, the less soluble adduct (obtained from III) should be represented by structure IX, and application of base to the adducts IX and X (*trans* isomer) should result in a more rapid elimination of



IX

a sulfinic acid from IX, where the favored *trans* elimination process is possible. However, solubility difficulties were again encountered along with the new complication of the principal final product being a saturated ether rather than an olefin. The reactions with base of the 1,2-bis-(*p*-tolylsulfonyl)-ethenes and their cyclopentadiene adducts proceed as in A and B, respectively.

$$C_7H_7SO_2CH{=}CHSO_2C_7H_7 \xrightarrow[\text{aq. alc.}]{\text{NaOH}} C_7H_7SO_2CH_3 + C_7H_7SO_2Na \quad (A)$$



(B)

Acknowledgment.—The authors are grateful to the Procter and Gamble Company for financial assistance in this work.

Experimental

trans-**1,2-Bis-(*p*-tolylmercapto)-ethene.**—Fifty grams of 1,2-bis-(*p*-tolylmercapto)-ethene (m.p. 91–92°) was distilled very slowly under nitrogen at 183–200° (5 mm.). The distillate solidified into a hard cake, which was broken up by heating with absolute alcohol. The hot alcohol solution was filtered and the residue was extracted with cold petroleum ether, leaving 20.7 g. of impure starting material, m.p. 83–85°. Chilling the alcohol filtrate yielded 20.0 g. of crystals, m.p. 52–55°. The resulting filtrate was combined with the petroleum ether extract and evaporated to give 6.0 g. of solid melting at 51–58°. Recrystallization of the latter two solids from absolute alcohol gave 16.6 g. (33.2%) of solid melting at 54.5–55.5°. A cooling curve of this material indicated that it was a pure compound.

Anal. Calcd. for $C_{16}H_{16}S_2$: C, 70.54; H, 5.92. Found: C, 70.68; H, 5.87.

trans-**1,2-Bis-(phenylmercapto)-ethene.**—Cusa and McCombie[7] prepared this compound by a procedure quite similar to the one which gave us the isomer melting at 30.5–31.5°. Instead of freezing out the product, they evaporated the reaction mixture under an air jet, added water, separated the oil that formed and distilled it at atmospheric pressure. By this procedure, any unreacted benzenethiol, which is present in the basic solution, will be converted by air oxidation[8] to diphenyl disulfide, which in turn will decompose on distillation at atmospheric pressure to diphenyl sulfide.[9] Thus, on one occasion, starting with *trans*-dichloroethylene, Cusa and McCombie's procedure yielded 49.7 g. (53.4%) of a distillate, which when oxidized with 30% hydrogen peroxide and glacial acetic acid gave 52.2 g. of crude and 43.0 g. of recrystallized diphenyl sulfone, m.p. 128–129° (lit.[10] 128–129°). This apparent unreactivity on the part of the starting dichloroethylene is avoided by using the *cis* isomer.[11] Furthermore, the initially obtained *cis*-1,2-bis-(phenylmercapto)-ethene (m.p. 30.5–31.5°) is distilled slowly at reduced pressure and under a nitrogen atmosphere. Crystallization of this distillate from petroleum ether gave the isomer melting at 62°.

Oxidation of the 1,2-Bis-(arylmercapto)-ethenes.—1,2-Bis-(*p*-tolylmercapto)-ethene (m.p. 91–92°, 2.72 g., 0.01 mole), prepared by the modification of Fromm and Seibert's method,[11] was placed in 50 ml. of glacial acetic acid; then 13.6 g. of 30% hydrogen peroxide was added. After one day the precipitate had disappeared. After five days a new precipitate had formed. On the sixth day, filtration yielded in two crops 2.89 g. (87%) of 1,2-bis-(*p*-tolylsulfonyl)-ethene, m.p. 151–152°, lit.[4] 149–150°.

By the same procedure 1.00 g. of the low-melting (52–55°) 1,2-bis-(*p*-tolylmercapto)-ethene yielded 0.83 g. (67%) of solid, m.p. 227–229°. Evaporation of the filtrate gave 0.28 g. (22%) of solid melting at 135–143°. These compounds are the *trans*[2] and *cis*[4] isomers of 1,2-bis-(*p*-tolylsulfonyl)-ethene, respectively.

Likewise, *cis*-1,2-bis-(phenylmercapto)-ethene (m.p. 30.5–31.5°) was converted (76%) to a sulfone having m.p. 101–101.5°.

Anal. Calcd. for $C_{14}H_{12}O_4S_2$: C, 54.52; H, 3.92. Found: C, 54.32; H, 3.92.

A mixture of 1 g. of the above material and 3.5 g. of zinc dust in 50 ml. of glacial acetic acid was refluxed for 3 hours to give a 68% yield of 1,2-bis-(phenylsulfonyl)-ethane.[12] A mixture with an authentic sample prepared from 1,2-bis-(phenylmercapto)-ethane by the method of Gilman and Beaber[13] melted without depression at 182.5–184°.

1,2-Bis-(phenylmercapto)-ethene (m.p. 62°, 1.00 g.) was placed in 18 ml. of glacial acetic acid; then, 5.0 g. of 30% hydrogen peroxide was added. After standing 6 days at room temperature the mixture was filtered. A white crystalline solid (1.11 g.) melting at 215–220° was obtained. Analysis of this material indicated that it was a mixture of disulfone and sulfoxide–sulfone. Further treatment of a portion of this product at reflux temperature for 4 hours with 30% hydrogen peroxide in glacial acetic acid gave 59% of solid melting at 229.5°. Admixture of this solid with a sample of 1,2-bis-(phenylsulfonyl)-ethene obtained in the manner described earlier[2] did not depress its melting point. In view of the isomorphism exhibited by sulfones and sulfoxides[14] as evidenced by the formation of continuous series of mixed crystals, an explanation for the above behavior is a rather easy oxidation to a disulfoxide or sulfoxide–sulfone, which is practically insoluble in the reaction mixture. Solubilizing the precipitate by application of heat or adding more solvent allows complete oxidation to the disulfone to occur.

Isomerization of *cis*-1,2-Bis-(arylsulfonyl)-ethenes.—1,2-Bis-(*p*-tolylsulfonyl)-ethene (m.p. 147–148°, 0.105 g.) was placed in a test-tube immersed in refluxing bromobenzene and heated for 24 hours. After cooling, the solid was broken up with 2–3 ml. of hot 95% alcohol. The residue which remained melted at 220–227°. Additional solid (m.p. 213–228°) was obtained from the cooled filtrate (total yield 0.04 g.). Chilling produced 0.01 g. of material melting at 145–147°. Because of the comparative insolubility of the high-melting isomer it is reasonable to assume that the material still in solution is the low melting, more soluble form. Thus, isomerization to approximately 40% completion occurred during the course of heating.

The reaction of the low melting 1,2-bis-(*p*-tolylsulfonyl)-ethene with anthracene[15] indicates a similar ratio of isomers under reaction conditions that resemble very closely those of the isomerization described here. The reaction of the high-melting 1,2-bis-(*p*-tolylsulfonyl)-ethene with anthracene,[2] however, gave a preponderance of one isomer (82%), indicating that the high melting isomer possessed greater stability toward thermal isomerization than the low melting 1,2-bis-(*p*-tolylsulfonyl)-ethene.

1,2-Bis-(phenylsulfonyl)-ethene (2.57 g., m.p. 99–100°) was placed in 6 ml. of glacial acetic acid and refluxed for 17 hours. After cooling, a little of the solid was removed on a spatula and dried on a porous plate; m.p. 99–100°. Glacial acetic acid (19 ml.) was added to this mixture, together with 2 ml. of 30% hydrogen peroxide. The mixture was returned to reflux for an additional 50 hours. The solution,

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

[8] J. Stenhouse, *Ann.*, **149**, 249 (1869).

[9] C. Graebe, *ibid.*, **174**, 189 (1874).

[10] R. Otto, *Ber.*, **18**, 249 (1885).

[11] Will be further described in a following paper.

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

[13] H. Gilman and N. J. Beaber, THIS JOURNAL, **47**, 1451 (1925).

[14] H. Rheinboldt and E. Giesbrecht, *ibid.*, **68**, 973 (1946).

[15] H. R. Snyder and D. P. Hallada, *ibid.*, **74**, 5595 (1952).

when chilled, yielded 0.74 g. (29%) of solid, m.p. 226–229°. A mixture with an authentic sample[2] of *trans*-1,2-bis-(phenylsulfonyl)-ethene melted over the same range.

Reaction of Base with *cis*- and *trans*-Bis-(*p*-tolylsulfonyl)-ethene.—A mixture of 2.354 g. of *cis*-bis-(*p*-tolylsulfonyl)-ethene, m.p. 146–148°, 25 ml. of alcohol and 100 ml. of 0.291 *N* sodium hydroxide was kept for 10 days at room temperature in a stoppered flask. The precipitate (0.2 g.) was removed and identified as the isomeric *trans*-bis-(*p*-tolylsulfonyl)-ethene by the undepressed melting point of a mixture with an authentic sample.[2] The filtrate was extracted with ether until coloration of the ether layer did not occur. The ether layer was dried over calcium chloride, and evaporated under a jet of dried air. A soft material, completely molten at 65°, was obtained. After two recrystallizations from petroleum ether (30–60°) a product (0.2 g.) melting at 85–87° was obtained. The melting point of a mixture with authentic[16] methyl *p*-tolyl sulfone (m.p. 88–88.5°) was 87–88°.

The aqueous layer was added to a boiling solution of 3 g. of mercuric chloride in 20 ml. of water.[17] A white solid formed, accompanied by a vigorous evolution of gas, which had the odor of sulfur dioxide. After the reaction had subsided, 200 ml. of water was added and the solution was boiled gently for one hour. The crude white solid, remaining after filtration was extracted with boiling xylene. Filtration and chilling of the xylene solution gave white needles, which when dried overnight at 100° (1 mm.) melted at 234–236° (sealed tube); lit.[18] 233°.

The solution resulting from the treatment of a sample of *trans*-bis-(*p*-tolylsulfonyl)-ethene with base as described above for the *cis* isomer, except that a 6-hour reflux period occurred after 51 hours of standing, yielded the same products as were obtained from the *cis* isomer, except that no *trans* isomer remained unreacted. The products were identified as before. Yields of purified products were: *p*-tolylmercuri chloride, 0.68 g. (34%); methyl *p*-tolyl sulfone, 0.75 g. (60%).

Reaction of 3,6-Methano-4,5-bis-(*p*-tolylsulfonyl)-1-cyclohexene with Base.—The adduct[2] of *trans*-bis-(*p*-tolylsulfonyl)-ethene and cyclopentadiene (4.68 g., 0.0116 mole) was added to a solution of sodium ethoxide prepared from 0.53 g. (0.0232 g. atom) of sodium and 60 ml. of absolute alcohol. The resulting mixture was refluxed for 0.5 hour, at which time all solid had disappeared. The solution was cooled and 10 ml. of water was added. The aqueous alcohol solution was extracted with 25-ml. portions of petroleum ether until evaporation of such a portion yielded only a very minute amount of solid. Refluxing the aqueous layer for 15 hours with 2 ml. of methyl iodide yielded in two crops, after treatment with sodium bisulfite and Norite, 1.63 g. (82%) of *p*-tolyl methyl sulfone, m.p. 87–88°, identified by the undepressed melting point of a mixture with an authentic sample.[16]

The petroleum ether extracts were evaporated and the residue was decolorized with Norite and recrystallized from 40 ml. of 95% alcohol to yield 2.28 g. of solid melting at 95.5°; m.p. 97.5–98° after three more recrystallizations.

Anal. Calcd. for $C_{16}H_{20}SO_3$: C, 65.72; H, 6.90; S, 10.97. Found: C, 66.27; H, 7.16; S, 11.79.

The action of base on analogous γ-disulfones is reported to yield a sulfinic acid and an alcohol or unsaturated compound.[19] Inasmuch as the preceding reaction was carried out in anhydrous media, the formation of an ether XI might be anticipated.

Dipole Moment Evidence for Configurations of *cis*- and *trans*-1,2-Bis-(*p*-tolylsulfonyl)-ethenes.[20]—A sample of 1,2-bis-(*p*-tolylsulfonyl)-ethene, m.p. 153–154°, that had been obtained by room temperature oxidation of the corresponding sulfide, was dried over phosphoric oxide for 8 hours at 1 mm. pressure and at room temperature. It was not recrystallized since recrystallization lowers the melting point to 149–150°, presumably by isomerization of a portion of the solid. Solubility of this isomer in benzene was 1.02 g. per 100 ml. of solution and in carbon tetrachloride the solubility was 0.19 g. per 100 ml. of solution.

The isomeric sulfone, m.p. 229.5–230°, was prepared by two recrystallizations from 95% alcohol of the relatively pure compound melting at 227–229°. It was dried under the same conditions as were used for the low-melting isomer. The solubility in benzene was 0.056 g. per 100 ml. of solution and in carbon tetrachloride was 0.012 g. per 100 ml. of solution.

"The isomer melting at 153–154° has a greater dipole moment than the isomer melting at 229.5–230°."[20]

Infrared Spectra of *cis*- and *trans*-1,2-Bis-(*p*-tolylmercapto)-ethene.[21]—Infrared spectra were obtained with a Perkin-Elmer Infrared Spectrometer, Model 21. The low-melting isomer was run as a 2% solution in carbon disulfide in a 0.598-mm. cell, whereas the high-melting, less soluble form was run as a 1% solution in a cell of 1.006-mm. thickness. The 10.36 μ band characteristic of *trans* isomers was not present in the spectrum of either isomer. However, the isomer melting at 54.5–55.5° exhibited a strong absorption at 10.8 μ, which may be the band expected, displaced by the presence of sulfur atoms adjacent to the double bond. Furthermore, a band at 7.48 μ occurred in the spectrum of the isomer melting at 93°. Colthup[22] shows a band correlation for *cis*-double bonds occurring at 7.15–7.4 μ.

LAFAYETTE, INDIANA

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[16] R. Otto, *Ber.*, **18**, 161 (1885).

[17] W. Peters, *ibid.*, **38**, 2569 (1905).

[18] F. C. Whitmore, F. H. Hamilton and N. Thurman, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 519.

[19] C. M. Suter, "The Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 744–746.

[20] These measurements were furnished through the courtesy of the personnel of the Experimental Station, E. I. du Pont de Nemours and Company.

[21] These determinations were kindly made by Dr. J. E. Callen, Miami Valley Laboratories, The Procter and Gamble Company.

[22] N. B. Colthup, *J. Opt. Soc. Amer.*, **40**, 397 (1950).