[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Stereospecific Reactions of Nucleophilic Agents with Acetylenes and Vinyl-type Halides. IV. The Stereochemistry of Nucleophilic Additions of Thiols to Acetylenic Hydrocarbons[1]

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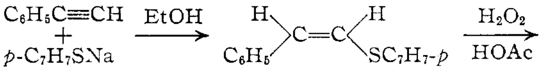
The base-catalyzed addition of *p*-toluenethiol to phenylacetylene and to 2-butyne yields *cis*-ω-styryl *p*-tolyl sulfide and 2-*p*-tolylmercapto-*trans*-2-butene, respectively. Phenylacetylene and methanethiol yield methyl *cis*-ω-styryl sulfide. *p*-Toluenethiol reacts with 1-hexyne to produce a mixture of 2-*p*-tolylmercapto-1-hexene and 1-*p*-tolylmercapto-1-hexene.

Base-catalyzed additions to acetylenes to form the corresponding vinyl compounds have been known for many years[3-6]; however, the stereochemistry of such additions has not been systematically studied.[6] There are several indications in the literature that such reactions may *not* produce a *mixture* of the possible *cis*- and *trans*-olefins. For example, an alkaline solution of *p*-nitrophenylacetylene and benzenethiol forms a pure phenyl *p*-nitro-ω-styryl sulfide, of undetermined geometry in 41% yield.[7] Also, only one of the two possible ω-ethoxystyrenes is formed when ethanol is added to phenylacetylene in the presence of sodium ethoxide.[8] Distillation at atmospheric pressure caused isomerization to a mixture of geometrical isomers.

Accordingly, a study of the stereochemistry of nucleophilic additions to simple acetylenes was begun. Recently, stereospecific *trans* nucleophilic additions across triple bonds were observed in the conversion (by alcoholic sodium *p*-toluenethiolate) of chloroacetylene and *p*-tolylmercaptoacetylene to *cis*-1-chloro-2-(*p*-tolylmercapto)-ethene and *cis*-bis-(*p*-tolylmercapto)-ethene, respectively.[9] This paper reports on base-catalyzed additions of thiols to phenylacetylene, 1-hexyne and 2-butyne.

Phenylacetylene.—Refluxing an alcoholic solution of phenylacetylene with sodium *p*-toluenethiolate resulted in a good yield of *cis*-ω-styryl *p*-tolyl sulfide (I). None of the *trans* isomer II was isolated.



I, m.p. 64–65.5°

cis-$C_6H_5CH{=}CHSO_2C_7H_7$-*p*
Ia, m.p. 76–77°

Kohler and Potter[10] obtained a mixture of *cis*-(I) and *trans*-(II) ω-styryl *p*-tolyl sulfides by the reaction of *p*-toluenethiol with phenylacetylene in the absence of any catalyst. They made no statements as to the geometry of their compounds. The ultraviolet spectra of the two vinyl sulfones prepared by the method of Kohler and Potter support our assignments of configuration to these compounds: Ia, $\lambda_{\max}$ 266 mμ, $\epsilon_{\max}$ 14.0×10^3; IIa (m.p. 121°), $\lambda_{\max}$ 276 mμ, $\epsilon_{\max}$ 25.9×10^3. With a number of β-substituted styrenes it has been found that the *trans* isomer has a somewhat higher $\lambda_{\max}$ and $\epsilon_{\max}$ than the *cis* isomer. Furthermore, "they differ more in intensity than in the position of absorption."[11] Also supporting these configurational assignments is the fact that the material we have designated as *trans*-ω-styryl *p*-tolyl sulfone (IIa) was prepared by the Friedel–Crafts reaction of *trans*-ω-styrenesulfonyl chloride[12-13] with toluene.[14]

With methanethiol, under similar reaction conditions, phenylacetylene yields methyl *cis*-ω-styryl sulfide (III). This sulfide was oxidized to a new

$$C_6H_5C{\equiv}CH + CH_3SNa \xrightarrow[\Delta]{EtOH} \textit{cis-}C_6H_5CH{=}CHSCH_3$$

III, oil, b.p. 107.6–115° (5 mm.)

$$\Big\downarrow{\scriptstyle H_2O_2,\ HOAc}$$

$$C_6H_5CH_2CH_2SO_2CH_3 \xleftarrow[H_2]{Pd} \textit{cis-}C_6H_5CH{=}CHSO_2CH_3$$

V, m.p. 88.5–89.5° IIIa, m.p. 66–67°

methyl ω-styryl sulfone (IIIa), whose structure was substantiated by reduction to the independently prepared methyl β-phenylethyl sulfone (V). Similarly, the isomeric IVa, m.p. 78–79°,[14] was also reduced (but slightly less readily than the 66.5° isomer) to V. The *trans* isomer[14] was prepared from *trans*-ω-styrenesulfonyl chloride[11,12] by the following sequence of reactions

$$\textit{trans-}C_6H_5CH{=}CHSO_2Cl \xrightarrow{Zn} \xrightarrow{Na_2CO_3} \xrightarrow{MeI} \textit{trans-}C_6H_5CH{=}CHSO_2CH_3$$

IVa

These configurational assignments are supported by spectral data. The higher-melting sulfone IVa has a strong infrared adsorption band at

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[1] Taken from the Ph.D. Thesis of J. A. Simms, Purdue University, 1956.

[2] Dow Chemical Company Fellow, 1954–1955.

[3] J. Reppe, "Acetylene Chemistry," P. B. Report 18852-S, pp. 28–68.

[4] J. W. Copenhaver and M. H. Bigelow, "Acetylene and Carbon Monoxide Chemistry," Reinhold Publishing Corp., New York, N. Y., 1949, pp. 33–84.

[5] J. A. Nieuwland and R. R. Vogt, "The Chemistry of Acetylene," Reinhold Publishing Corp., New York, N. Y., 1945, pp. 129–135.

[6] R. A. Raphael, "Acetylenic Compounds in Organic Synthesis," Academic Press, Inc., New York, 1955, p. 43.

[7] S. J. Cristol, *et al.*, THIS JOURNAL, **76**, 4558 (1954).

[8] C. Dufraisse and R. Chaux, *Bull. soc. chim.*, [4] **39**, 905 (1926).

[9] W. E. Truce, M. M. Boudakian, R. F. Heine and R. J. McManimie, THIS JOURNAL, **78**, 2746 (1956); W. E. Truce, J. A. Simms and M. M. Boudakian, *ibid.*, **78**, 695 (1956).

[10] E. P. Kohler and H. A. Potter, *ibid.*, **57**, 1316 (1935).

[11] F. A. Miller in H. Gilman's "Organic Chemistry," Vol. III, Chapt. 2, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 168.

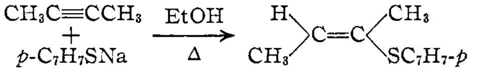
[12] A. P. Terent'ev, R. A. Gracheva and Z. F. Shcherbatova, *Doklady Akad. Nauk S.S.S.R.*, **84**, 975 (1952); *C. A.*, **47**, 3262 (1953).

[13] C. S. Rondestvedt and J. C. Wygant, THIS JOURNAL, **73**, 5785 (1951).

[14] W. E. Truce, J. A. Simms and H. E. Hill, *ibid.*, **75**, 5411 (1953).

10.35 μ, a band usually assigned to the *trans*-hydrogens in 1,2-disubstituted ethylenes.[15] The other *cis* and *trans* bands were masked by adsorptions characteristic of the sulfone and styrene systems, or by the Nujol bands inherent in the method used to obtain the spectra. The ultraviolet spectral data also substantiate the assignment of the *trans* structure to the methyl ω-styryl sulfone melting at 78°: IIIa, λ_{max} 261 mμ, ϵ_{max} 19.9 × 10^3; IVa, λ_{max} 264 mμ, ϵ_{max} 23.7 × 10^3.

2-Butyne.[16]—Sodium *p*-toluenethiolate was treated with 2-butyne[16] in ethanol solution to form a monoadduct characterized by its elemental analysis and infrared spectrum as 2-*p*-tolylmercapto-*trans*-2-butene (VI).


VI

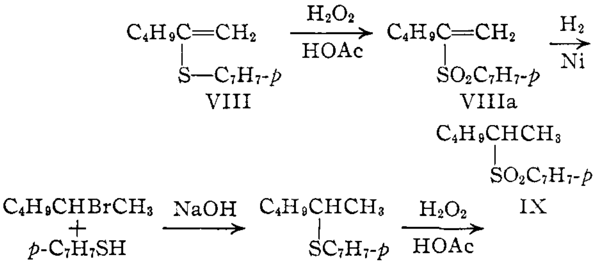
The geometry was assigned by analogy with the addition of mercaptans to phenylacetylene where *trans* addition was demonstrated. This assignment is strengthened by the occurrence of an infrared adsorption band at 7.70 mμ in the spectrum of the adduct. *trans*-2-Butene[17] and 2-chloro-*trans*-2-butene[18] both have a band in their spectra at 7.80 mμ while the spectra of the corresponding *cis* compounds do not show adsorption bands in this region.

1-Hexyne.—Two products were isolated and characterized when sodium *p*-toluenethiolate was treated with 1-hexyne in ethanol solution. Approximately one-fifth of the product was found to be 1-*p*-tolylmercapto-1-hexene (VII), while the remainder was 2-*p*-tolylmercapto-1-hexene (VIII). The total yield of adducts was 89.5%.

$$C_4H_9C{\equiv}CH + C_7H_7SNa \xrightarrow{EtOH} \begin{array}{c} C_4H_9CH{=}CHSC_7H_7 \\ \text{VII} \\ (C_4H_9)(C_7H_7S)C{=}CH_2 \\ \text{VIII} \end{array}$$

The two components were separated by slow distillation through a Todd column. The material which was characterized as 2-*p*-tolylmercapto-1-hexene (VIII) boiled at 140–141.5° (10 mm.), $n^{20}D$ 1.5475 ± 0.0010. The fractions containing 1-*p*-tolylmercapto-1-hexene (VII) boiled at 150–160° (10 mm.), $n^{20}D$ 1.5545 ± 0.0010. The infrared spectra of the twelve cuts made during this distillation did not give any conclusive evidence as to the nature of the two materials, although as the distillation progressed a weak peak at 11.25 μ disappeared as a peak at 10.50 μ was intensified. The band at 11.25 μ probably indicates the $>C{=}CH_2$ grouping (reported[19] 11.24 ± 0.06 μ, while the band at 10.50 μ suggests the presence of a *trans*-1,2-disubstituted ethylene (reported[19] 10.20–10.35 μ).

The following reaction sequence shows the method used to identify the lower boiling sulfide as 2-*p*-tolylmercapto-1-hexene (VIII)

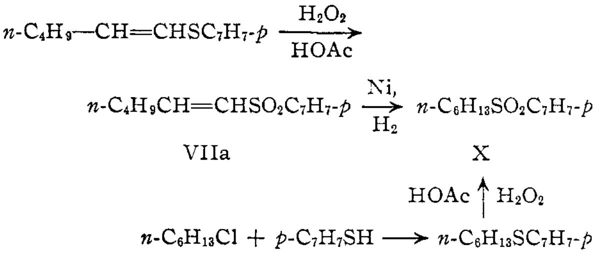


$$\underset{\text{VIII}}{\underset{S-C_7H_7\text{-}p}{C_4H_9C{=}CH_2}} \xrightarrow[HOAc]{H_2O_2} \underset{\text{VIIIa}}{\underset{SO_2C_7H_7\text{-}p}{C_4H_9C{=}CH_2}} \xrightarrow[Ni]{H_2} \underset{SO_2C_7H_7\text{-}p}{C_4H_9CHCH_3}$$

$$\begin{array}{c} C_4H_9CHBrCH_3 \\ + \\ p\text{-}C_7H_7SH \end{array} \xrightarrow{NaOH} \underset{SC_7H_7\text{-}p}{C_4H_9CHCH_3} \xrightarrow[HOAc]{H_2O_2} \text{IX}$$

The infrared spectrum of the reduction product was identical with the spectrum of the 2-*p*-tolylsulfonylhexane (IX) prepared from 2-bromohexane and *p*-toluenethiol.

The higher boiling component was characterized as 1-*p*-tolylmercapto-1-hexene in a similar way



$$n\text{-}C_4H_9{-}CH{=}CHSC_7H_7\text{-}p \xrightarrow[HOAc]{H_2O_2}$$

$$\underset{\text{VIIa}}{n\text{-}C_4H_9CH{=}CHSO_2C_7H_7\text{-}p} \xrightarrow[H_2]{Ni,} \underset{\text{X}}{n\text{-}C_6H_{13}SO_2C_7H_7\text{-}p}$$

$$\text{HOAc} \uparrow H_2O_2$$

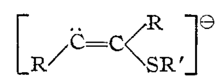
$$n\text{-}C_6H_{13}Cl + p\text{-}C_7H_7SH \longrightarrow n\text{-}C_6H_{13}SC_7H_7\text{-}p$$

The spectrum of the reduction product was virtually identical with the spectrum of *n*-hexyl *p*-tolyl sulfone (X). The *cis* or *trans* nature of the initially formed 1-*p*-tolylmercapto-1-hexene (VII) is unknown since its separation from the 2-*p*-tolylmercapto-1-hexene (VIII) involved extended heating at reduced pressure. However, the 1-*p*-tolylmercapto-1-hexene (VII) separated by distillation had a peak in its infrared spectrum at 10.5 μ, which was not present in the spectrum of the undistilled mixture. This suggests that the *cis* compound was present in the mixture and that it was isomerized to the *trans*-vinyl sulfide during distillation.

Discussion

In the reactions of phenylacetylene and 2-butyne with the thiolates only the isomers resulting from *trans* addition were produced. The homogeneity of the unpurified products indicates that the other possible adducts were formed in low yield if at all. The orientation obtained in these additions is consistent with the nucleophilic character of the addendum and the electronegative character of a phenyl substituent as compared with a methyl substituent.

If the reaction is stepwise[20] there should be an intermediate configurationally stable carbanion



R = CH_3, C_6H_5 or H
R′ = *p*-C_7H_7 or CH_3

The indicated stereochemistry (and not *cis* displacement) would be expected on the basis that in the transition state the negative charge (unshared electron pair) and the negatively charged sulfur group would tend to be separated as far as possible from each other. This postulated configurational

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(15) Reference 11, p. 144.

(16) J. Wislicenus and P. Schmidt, *Ann.*, **313**, 220 (1900).

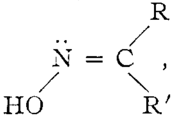
(17) American Petroleum Institute, Research Project No. 44, Spectra 21 and 22.

(18) Purdue University Infrared Laboratory, unpublished work.

(19) Reference 11, p. 144.

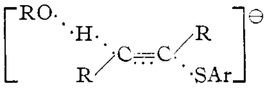
(20) S. I. Miller and G. Shkapenko, THIS JOURNAL, **77**, 5038 (1955).

stability of a "vinyl" carbanion is reminiscent of the geometry of the isoelectronic oximes,



, and of the retention of configuration by lithium compounds formed from vinyl halides.[21,22] However, any analogy between this last result and our results is weakened by the considerable covalent character of a carbon–lithium bond.[23]

Another route by which these stereospecific *trans* nucleophilic additions may be proceeding is a concerted process, involving the transition state



At present, evidence is being sought to permit choosing between these two alternatives.

Experimental[24]

***cis*-ω-Styryl *p*-Tolyl Sulfide** (I).—*p*-Toluenethiol (12.75 g., 0.103 mole) was added to a solution prepared from 2.37 g. (0.13 mole) of sodium and 100 ml. of absolute ethanol. Freshly distilled phenylacetylene[25] (10.0 g., 0.098 mole) was then added and, after 15 hours at reflux, the resulting brown solution was poured into water. When this mixture was cooled in the refrigerator a light yellow solid precipitated, which, after drying in a vacuum desiccator, weighed 17.2 g., and melted at 59–63°. It was recrystallized from methanol in three fractions: (1) wt. 10.0 g., m.p. 64–64.5°; (2) wt. 3.4 g., m.p. 63.5–65.5°; (3) wt. 2.5 g., m.p. 60–64°. Ether extraction of the water filtrate yielded 0.56 g. of adduct having m.p. 62–64°, after recrystallization from methanol (reported[10] m.p. 65°), thereby increasing the yield to 79%. A sample which was stored in a sealed bottle in the dark for several months liquefied. This was probably because of partial isomerization to the *trans* compound, m.p. 44°. Some *p*-toluenethiol, wt. 0.34 g., m.p. 40–42° (undepressed by an authentic sample), was recovered by acidifying the water filtrate and extracting with ether.

The presence or absence of 1% of the free radical inhibitor N-phenyl-β-naphthylamine had no effect on the yield or composition of the adduct produced in the reaction of sodium *p*-toluenethiolate with phenylacetylene.

***cis*-ω-Styryl *p*-Tolyl Sulfone** (Ia).—To a cooled solution of 3.37 g. of *cis*-ω-styryl *p*-tolyl sulfide in 25 ml. of glacial acetic acid was added 6.0 ml. of 30% hydrogen peroxide. This mixture was heated for one hour on the steam-plate. A white solid formed when the mixture was poured into ice-water; m.p. 74–76°, wt. 3.31 g. (yield 87%). Recrystallization from methanol gave 2.50 g. of product, m.p. 76–77° (reported[10] m.p. 77°).

All the ultraviolet spectra mentioned in this paper were determined in 95% ethyl alcohol on a Cary recording spectrophotometer, model 10-11M.

Methyl *cis*-ω-Styryl Sulfide (III).—To a solution of 7.15 g. (0.309 mole) of sodium in 250 ml. of ethanol was added 14.9 g. (0.309 mole) of methanethiol. Phenylacetylene (30 g., 0.294 mole) was rapidly added and the mixture was refluxed for 23 hours. Most of the ethanol was then stripped off at reduced pressure and the residue was poured into water. This mixture was extracted with ether and the extract dried over sodium sulfate. After the ether had been stripped off, the residue was distilled: (1) wt. 1.69 g., b.p. 93–100° (4 mm.); (2) wt. 29.89 g., b.p. 100–104° (4 mm.); (3) wt. 2.54 g., b.p. 104–105° (4 mm.). Fractions 2 and 3 represent a combined yield of 73%. A portion of fraction 2 was distilled at 101.5° (4 mm.).

Anal. Calcd. for $C_9H_{10}S$: C, 71.95; H, 6.71. Found: C, 71.28; H, 6.88.

Methyl *cis*-ω-Styryl Sulfone (IIIa).—To a solution of 3.0 g. (0.02 mole) of methyl *cis*-ω-styryl sulfide in 25 ml. of glacial acetic acid was added 6.8 ml. (0.06 mole) of 30% hydrogen peroxide. After heating for 1.5 hours on the steam-plate the solution was diluted with water and cooled to yield 2.41 g. (66%) of methyl *cis*-ω-styryl sulfone, m.p. 64.5–66°. An analytical sample, m.p. 66–67°, was obtained by one recrystallization from 60–70° petroleum ether.

Anal. Calcd. for $C_9H_9SO_2$: C, 59.64; H, 4.97. Found: C, 59.44; H, 4.94.

Oxidation at room temperature for 4 days gave essentially the same result. No evidence for isomerization during oxidation was encountered.

The infrared spectra of methyl *cis*-ω-styryl sulfone (IIIa) and the corresponding *trans* compound[9] IVa, determined as Nujol mulls with the Perkin-Elmer 21 recording infrared spectrophotometer, were: (IIIa) 3.50(m), 6.25(m), 7.10 (m), 7.83(s), 8.55(v.w.), 8.90(s), 9.30(w), 10.15(m), 12.00 (w), 13.15(s), 14.00(w), 14.30–14.75(s)μ; (IVa) 3.50(m), 6.25(m), 6.95(s), 7.35(w), 7.90(s), 8.45(v.w.), 9.05(s), 10.15(m), 10.35(s), 12.15(m), 12.55(s), 13.15(s), 13.50(s), 14.60(m) μ.

Reduction of Methyl *cis*-ω-Styryl Sulfone.—A solution of 1.28 g. of methyl *cis*-ω-styryl sulfone in 100 ml. of absolute ethyl alcohol was mixed with 0.4 g. of 10% palladium-on-charcoal[25a] and shaken with hydrogen at 30 p.s.i. for 1.5 hours. Evaporation of the filtered solution yielded 1.22 g. of product, m.p. 88–89°. This material did not depress the m.p. of an authentic sample of methyl β-phenylethyl sulfone (m.p. 88.5–89.5°).

Reduction of Methyl *trans*-ω-Styryl Sulfone.—A solution of 4.8 g. of methyl *trans*-ω-styryl sulfone[13] (m.p. 79–80°) in 150 ml. of absolute ethanol was mixed with 1 g. of 10% palladium-on-charcoal[25a] and hydrogenated at 20 p.s.i. in a Parr hydrogenator for 1.5 hours. The product was recovered as usual and recrystallized in two fractions from aqueous ethanol: (1) wt. 4.60 g., m.p. 76–78°; (2) wt. 0.17 g., m.p. 85–86.5°. Fraction 1 was re-hydrogenated for 12 hours at 30 p.s.i. using the same quantity of catalyst and solvent. The material obtained by evaporating the ethanol melted at 88–90°. It was recrystallized from aqueous ethanol in two fractions: (1) wt. 2.15 g., m.p. 89–90°; (2) wt. 0.08 g., m.p. 89–90°. The product did not decolorize potassium permanganate in acetone and gave no melting point depression with a known sample of methyl β-phenylethyl sulfone (m.p. 88.5–89.5°).

Methyl β-Phenylethyl Sulfone (V).—The method used to prepare ethyl β-phenylethyl sulfide[26] was used to prepare the corresponding methyl sulfide. Sodium hydroxide (8.8 g., 0.22 mole) was dissolved in 100 ml. of absolute ethyl alcohol. Methanethiol (10.6 g., 0.22 mole) was added and the solution was heated to reflux. β-Phenylethyl bromide[27] (40.7 g., 0.22 mole) was added at a rate which maintained reflux. After an additional 30-minute reflux period, most of the solvent was stripped off. The residue was poured into water and the product extracted with ether. The oil recovered from the dried extract was distilled at reduced pressure in two fractions: (1) b.p. 95–98° (6 mm.), wt. 5.8 g.; (2) b.p. 98–100° (6 mm.), wt. 21.29 g.; total yield of methyl β-phenylethyl sulfide, 80%.

The sulfone was prepared by dissolving 10 g. (0.066 mole) of the sulfide in 100 ml. of glacial acetic acid and adding 23 ml. (0.198 mole) of 30% hydrogen peroxide. This mixture was heated at reflux for 1.5 hours. The solid (wt. 9.7 g., m.p. 87.5–89°), which precipitated when the cooled solution was poured into ice-water, was filtered, washed several times with water, and dried in a vacuum desiccator. It was recrystallized from dilute ethanol to yield 8.0 g. (80%) of methyl β-phenylethyl sulfone, m.p. 88.5–89.5°.

2-*p*-Tolylmercapto-*trans*-2-butene (VI).—Sodium (2.11 g., 0.092 mole) was added to a cooled mixture of 45 ml. of absolute ethanol and 11.5 g. (0.092 mole) of *p*-toluenethiol. This solution was placed in a Carius tube along with a solution of 5.0 g. (0.092 mole) of 2-butyne[16,28] in 10 ml. of absolute ethanol. The tube was flushed with nitrogen, sealed, and heated for 96 hours at 150°. After cooling, it was

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[21] A. S. Dreiding and P. J. Pratt, This Journal, **76**, 1902 (1954).

[22] E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 2078 (1951).

[23] M. T. Rogers and A. Young, This Journal, **68**, 2748 (1946).

[24] All melting points are uncorrected.

[25] Eastman Organic Chemicals, b.p. 72.5–74° (80 mm.).

[25a] *Organic Syntheses*, Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 685.

[26] E. A. Fehnel and M. Carmack, This Journal, **71**, 92 (1949).

[27] A. W. Dox, *ibid.*, **46**, 2844 (1924).

[28] The 2-butyne, b.p. 27°, was supplied by M. Boudakian of this Laboratory.

opened, the solution was concentrated, mixed with water, and ether-extracted to yield 10.0 g. of yellow oil. This was distilled: (1) b.p. 60–83° (2 mm.), wt. 0.93 g.; (2) b.p. 83-86° (2 mm.), wt. 7.53 g., n^{20}_{D} 1.5634; (3) b.p. 83° (2 mm.), wt. 0.47 g. The recovered *p*-toluenethiol from the acidified wash water amounted to 0.7 g.; yield of crude adduct, 65%. An analytical sample was taken from fraction 2.

Anal. Calcd. for $C_{11}H_{14}S$: C, 74.10; H, 7.91. Found: C, 73.82; H, 7.87.

The infrared absorption bands and their relative intensities for 2-*p*-tolylmercapto-*trans*-2-butene were: 3.45(s), 5.30(v.w.), 6.12(w), 6.25(w), 6.73(s), 7.00(s), 7.30(m), 7.70(s), 8.30(w), 8.50(v.w.), 8.75(w), 9.20(m), 9.85(s), 11.10(m), 12.00(s), 14.20(w), 14.85(w) μ.

Addition of *p*-Toluenethiol to 1-Hexyne.[29]—A solution of sodium *p*-toluenethiolate was prepared by dissolving 5.60 g. (0.224 mole) of sodium in a mixture of 30.2 g. (0.244 mole) of *p*-toluenethiol and 90 ml. of absolute ethanol. This solution was divided equally between two carius tubes and 10 g. (0.122 mole) of 1-hexyne[29] was washed into each tube with 5 ml. of ethanol. After 5 days at 160°, the combined contents of the tubes were concentrated and the liquid residue was mixed with water. The product was extracted with ether, the extract dried over calcium chloride, and then evaporated under an air jet to yield 33.4 g. of light yellow oil. The recovered *p*-toluenethiol, obtained by extracting the acidified water layer with 30-60° petroleum ether, weighed 7.3 g. and had m.p. 42–43.5°. Based on consumed *p*-toluenethiol the yield of adduct was 89.5%. Distillation of this product through a 4″ Vigreux column gave 0.46 g. of a 1-*p*-tolymercapto-1-hexene having b.p. 109–110° (0.8 mm.), n^{20}_{D} 1.5542. The lower cuts, b.p. 97–109° (0.6 mm.), n^{20}_{D} 1.5475 ± 0.0010, wt. 30.76 g., were recombined and slowly distilled through a Todd column using the 5 mm. i.d. Monel spiral and a 5:1 reflux ratio to give the following fractions [fraction number, b.p. °C. (mm.), wt. g., $n^{20.5}_{\mathrm{D}}$]: 1, 133–134 (10), 1.17, 1.5450; 2, 137–140 (10), 1.12, 1.5452; 3, 140–142.5 (10), 2.51, 1.5470; 4, 142.5 (10), 4.18, 1.5475; 5, 141.5 (9), 4.72, 1.5488; 6, 141.5 (9), 3.54, 1.5489; 7, 141.5 (9), 1.85, 1.5492; 8, 141.5–145 (9), 1.43, 1.5492; 9, 145 (9), 1.86, 1.5509; 10, 145–150 (9), 0.93, 1.5523; 11, 150–156 (9), 0.94, 1.5540; 12, 156–160 (9), 0.59, 1.5548; total wt. 24.84 g.

Three changes occur in the infrared spectra in going from fractions 1 to 12. The intensity of a weak peak at 11.50 μ decreases to the vanishing point. A peak at 10.50 μ changes in appearance and increases in intensity to a medium value. A very weak peak appears at 5.85 μ as a peak of similar intensity at 6.13 μ vanishes.

2-*p*-Tolylsulfonyl-1-hexene (**VIIIa**).—2-*p*-Tolymercapto-1-hexene (VIII, fractions 3–6 from the above addition reaction, wt. 12.4 g., 0.0605 mole) was dissolved in 100 ml. of glacial acetic acid and 27.5 ml. (0.242 mole) of 30% hydrogen peroxide, was added dropwise. This solution was heated 3 hours on a steam-cone, the excess peroxide destroyed by the addition of a small amount of manganese dioxide, and most of the acetic acid stripped off under vacuum. The residue was mixed with water and the product extracted with ether. After drying over calcium chloride, evaporation of the ether yielded a yellow oil, which was distilled at reduced pressure: (1) b.p. 140–164° (0.8 mm.), wt. 1.33 g., n^{20}_{D} 1.5335; (2) b.p. 162-164° (0.6–0.8 mm.), wt. 3.74 g., $n^{20.5}_{\mathrm{D}}$ 1.5348; (3) b.p. 160–164° (0.5 mm.), wt. 2.47 g., n^{20}_{D} 1.5360. An analytical sample had b.p. 145° (0.30 mm.), n^{20}_{D} 1.5358.

Anal. Calcd. for $C_{13}H_{18}SO_2$: C, 65.51; H, 7.61. Found: C, 65.26; H, 7.76.

Hydrogenation of 2-*p*-Tolylsulfonyl-1-hexene.—2-*p*-Tolylsulfonyl-1-hexene (VIIIa, wt. 4.0 g., $n^{20.5}_{\mathrm{D}}$ 1.5348 ± 10) could not be hydrogenated at 40 p.s.i. in glacial acetic acid solution in the presence of 3.2 g. of 10% palladium-on-charcoal. The recovered olefin (wt. 3.1 g., $n^{20.2}_{\mathrm{D}}$ 1.5334) was hydrogenated at 60° and 58 p.s.i. using ethyl alcohol as the solvent and 3 g. of Raney nickel catalyst. The product weighed 2.14 g., and slowly decolorized an acetone solution of potassium permanganate. It was distilled at 143–146° (0.3 mm.) to give 1.68 g. of oil having n^{20}_{D} 1.5228. The infrared spectrum of this material is identical with the spectrum of 2-*p*-tolylsulfonylhexane, n^{20}_{D} 1.5200.

Anal. Calcd. for $C_{13}H_{20}SO_2$: C, 64.96; H, 8.38. Found: C, 64.49; H, 8.31.

1-*p*-Tolylsulfonyl-1-hexene (**VIIa**).—1-*p*-Tolylsulfonyl-1-hexene (VII, fractions 10–12, wt. 1.74 g.) was dissolved in 30 ml. of glacial acetic acid; 6 ml. of 30% hydrogen peroxide was added, and the solution was heated on the steam-plate for 2 hours. The usual workup yielded 1.74 g. of oil which was distilled to yield 1.14 g. of 1-*p*-tolylsulfonyl-1-hexene, b.p. 155–165° (0.3 mm.), n^{20}_{D} 1.5328.

Reduction of 1-*p*-Tolylsulfonyl-1-hexene.—The product (1.1 g.) from the above oxidation was dissolved in absolute ethanol and shaken with hydrogen at 60 p.s.i. in the presence of 1 g. of Raney nickel at 60° for 24 hours. The reduced material (wt. 0.93 g.) was recovered by filtering off the catalyst and evaporating the ethanol. Its ethanol solution slowly decolorized dilute potassium permanganate. Distillation yielded 0.69 g. of product, b.p. 147–155° (0.25 mm.), $n^{20.5}_{\mathrm{D}}$ 1.5190.

The infrared spectrum of the reduction product corresponds quite closely to the spectrum of *n*-hexyl *p*-tolyl sulfone, $n^{20.5}_{\mathrm{D}}$ 1.5166. However, peaks were present in the spectrum of the reduction product at 3.0 and at 5.82 μ, which were not present in the spectra of *n*-hexyl *p*-tolyl sulfone or 2-*p*-tolylsulfonylhexane.

***n*-Hexyl *p*-Tolyl Sulfone** (**X**).—*n*-Hexyl *p*-tolyl sulfide was prepared in 75% yield by treating a solution of sodium *p*-toluenethiolate prepared from 5.7 g. (0.248 mole) of sodium, 30.8 g. (0.248 mole) of *p*-toluenethiol and 250 ml. of ethanol with 30.0 g. (0.248 mole) of freshly distilled *n*-hexyl chloride (b.p. 132–133°). The mixture was refluxed for 3 hours, filtered and concentrated under an air jet. Cooling yielded a solid that melted at −3.5°. It was distilled in three fractions: (1) b.p. 110–121° (1.5–2 mm.) wt. 2.63 g., $n^{20.3}_{\mathrm{D}}$ 1.5300; (2) b.p. 120–121° (1.5–2 mm.), wt. 32.30 g., $n^{20.3}_{\mathrm{D}}$ 1.5298; (3) b.p. 121–123° (1.5–2 mm.), wt. 3.75 g., $n^{20.3}_{\mathrm{D}}$ 1.5302.

The corresponding sulfone was prepared in 84% yield by oxidizing 20.0 g. (0.096 mole) of *n*-hexyl *p*-tolyl sulfide with 33 ml. (0.29 mole) of 30% hydrogen peroxide dissolved in 200 ml. of glacial acetic acid. After 5 hours heating on a steam-cone, most of the acetic acid was stripped off at reduced pressure. When the residue was mixed with water and cooled a white solid formed. It was recrystallized from a mixture of ether and petroleum ether (b.p. 37°) in two fractions: (1) wt. 14.22 g., m.p. 34°; (2) wt. 5.09 g., semisolid. Fraction 1 was distilled at reduced pressure: (1) b.p. 140-170° (0.3–0.4 mm.), wt. 5.54 g., n^{20}_{D} 1.5168; (2) b.p. 170–175° (0.3–0.4 mm.), wt. 3.92 g., n^{20}_{D} 1.5166; (3) b.p. 175–182° (0.3–0.4 mm.), wt. 2.24 g., n^{20}_{D} 1.5166.

The reported b.p.[30] of *n*-hexyl *p*-tolyl sulfone is 158–159° (0.8 mm.).

2-*p*-Tolylsulfonylhexane (**IX**).—2-*p*-Tolylmercaptohexane was prepared in 76% yield from 2-bromohexane[31] using the same procedure given above for *n*-hexyl *p*-tolyl sulfide; b.p. 106–109° (1.52 mm.), n^{20}_{D} 1.5272. 2-*p*-Tolylsulfonylhexane was prepared in 78% yield by oxidizing 2-*p*-tolylmercaptohexane in the same way as was reported in the preparation of *n*-hexyl *p*-tolyl sulfone; b.p. 158–164° (0.3 mm.), n^{20}_{D} 1.5200.

Infrared Spectra of the Hexyl *p*-Tolyl Sulfones.—Since no marked differences appear in the spectra of the two sulfones below 9 μ only the region from 9.0 to 15 μ is given. *n*-Hexyl *p*-tolyl sulfone: 9.20(s), 9.65(v.w.), 9.85(w), 12.60(s), *13.10*(s), 14.00(m), 14.50(w) μ. 2-*p*-Tolylsulfonyl hexane: 9.25(s), 9.85(w), *11.45*(w), 12.60(s), 13.75–14.05(s), 14.60(m) μ. The italicized peaks are characteristic of the two compounds.

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[31] Prepared by treating a benzene solution of 2-hexanol with phosphorus tribromide; b.p. 138.5–140°, n^{20}_{D} 1.4440.