tassium hydroxide extracts) was acidified with concd. hydrochloric acid, extracted with petroleum ether (30–60°), dried over magnesium sulfate and evaporated to give a solid, m.p. 39.0–41.0°, wt. 0.30 g. (89.3% recovery of *p*-toluenethiol).

Reaction of *p*-Tolylmercaptoacetylene (IV)[38] with Sodium *p*-Toluenethiolate. A.—The following reactants were heated to reflux for 24 hours under a nitrogen atmosphere: freshly distilled *p*-tolylmercaptoacetylene (IV) (0.50 g., 0.00338 mole), *p*-toluenethiol (0.42 g., 0.00338 mole), sodium (0.08 g., 0.00338 mole) and absolute ethanol (25 ml.). The reaction mixture was concentrated, diluted with water, extracted with petroleum ether (30–60°), the extracts evaporated and recrystallized from 95% ethanol to give a product (wt. 0.71 g., 77.2% conversion to V) melting at 91.0–91.5°. A mixed melting point determination with an authentic sample of *cis*-1,2-bis-(*p*-tolylmercapto)-ethene (V) showed no depression (m.p. 91.0–92.0°).

The remainder of the reaction mixture was acidified with concd. hydrochloric acid, extracted with petroleum ether (30–60°), the extracts dried over magnesium sulfate and evaporated to give a solid, m.p. 40.0–41.0°, wt. 0.05 g., which represented a 12.2% recovery of *p*-toluenethiol.

B.—An identical experiment was concurrently run, except that diphenylamine, a free radical inhibitor (0.02 g., 0.06 wt. %), was used. Following the usual work-up procedure, 0.69 g. (74.9% conversion) of *cis*-1,2-bis-(*p*-tolylmercapto)-ethene, m.p. 91.0–92.0°, was obtained.

From the acidified reaction mixture, 0.05 g. (12.2%) of *p*-toluenethiol was recovered.

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LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Stereospecific Reactions of Nucleophilic Agents with Acetylenes and Vinyl-type Halides. II. The Mechanism of the Base-catalyzed Reaction of Vinylidene Chloride with Thiols

BY WILLIAM E. TRUCE AND MAX M. BOUDAKIAN[1]

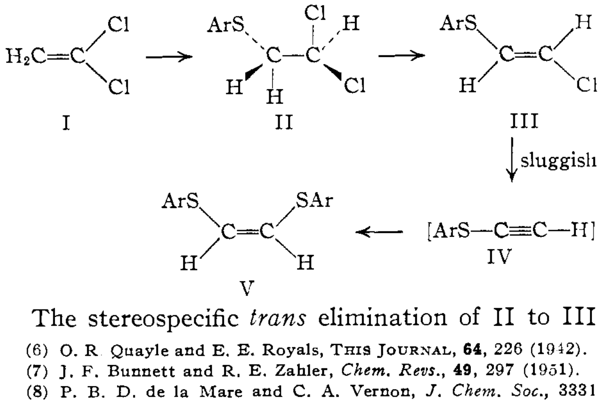
RECEIVED OCTOBER 21, 1955

Vinylidene chloride (I) reacts with sodium *p*-toluenethiolate to give exclusively *cis*-1,2-bis-(*p*-tolylmercapto)-ethene (V). Evidence is provided for a mechanism. Depending on the conditions employed, the reaction can be controlled so that 1,1-dichloro-2-(*p*-tolylmercapto)-ethane (II), *trans*-1-chloro-2-(*p*-tolylmercapto)-ethene (III) or V can be isolated. Intermediates II, III and *p*-tolymercaptoacetylene (IV, independently synthesized) give V on treatment with sodium *p*-toluenethiolate. The conversion of III to V was shown to be base-catalyzed.

Since the geometrically isomeric dichloroethylenes exhibited a great difference in reactivity toward base-catalyzed reactions with thiolates[2,3] and sulfites,[4] it became of interest to study the behavior of the isomeric vinylidene chloride with these nucleophilic agents. Potassium sulfite reacted with vinylidene chloride to give potassium 1,1,2-ethanetrisulfonate.[4] In the present work, the reaction of vinylidene chloride with an arylthiolate was investigated. Previously, it had been demonstrated that *cis*-dichloroethylene reacted with sodium *p*-toluenethiolate to give *cis*-1,2-bis-(*p*-tolylmercapto)-ethene (V) and it was further shown that the first step in this conversion involved an elimination to chloroacetylene.[2]

In the present study, vinylidene chloride (I) also gave V in almost quantitative yield. By analogy to the reaction between *cis*-dichloroethylene and the thiol reagent,[2,3] an elimination–addition mechanism seemed probable. However, FitzGibbon[5] found that vinylidene chloride did not react with alkaline mercuric cyanide; in contrast, *cis*-dichloroethylene gave mercuric bis-(chloroacetylide), $\mathrm{Hg(C{\equiv}C{-}Cl)_2}$, under the same conditions. Attempts in this laboratory to prepare mercuric bis-(chloroacetylide) from vinylidene chloride under a variety of conditions were also unsuccessful.

By controlling the reaction conditions, one can isolate either of the products of an initial addition–elimination sequence, 1,1-dichloro-2-(*p*-tolylmercapto)-ethane (II) and *trans*-1-chloro-2-(*p*-tolylmercapto)-ethene (III), thus providing further evidence against an elimination–addition mechanism. Intermediate II was identified by elemental analysis of its sulfone. The orientation of the attack by the highly nucleophilic arylthiolate ion[6–10] may be explained as due to a polarizing influence (inductive effect) of the chlorine atoms on an incipient carbanion, $\mathrm{Ar\ddot{S}CH_2\overset{(-)}{C}Cl_2}$, and/or on the olefinic group in the starting vinylidene chloride (thereby facilitating nucleophilic attack at the methylene group). Intermediate II was converted to V by treatment with thiolate in the presence of sodium ethoxide.



The stereospecific *trans* elimination of II to III

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[1] Abstracted from the Ph.D. Thesis of Max M. Boudakian, Purdue University, 1956. Presented at the Dallas, Texas, Meeting of the American Chemical Society, April, 1956.

[2] W. E. Truce, M. M. Boudakian, R. F. Heine and R. J. McManimie, THIS JOURNAL, **78**, 2746 (1956).

[3] W. E. Truce and R. J. McManimie, *ibid.*, **76**, 5745 (1954).

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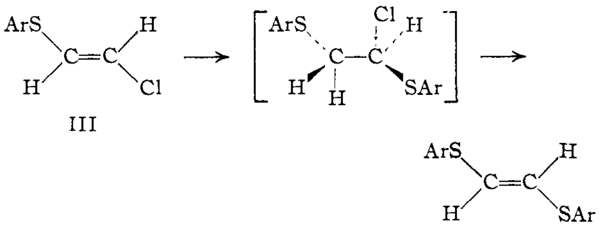
is an excellent illustration of the *cis* effect,[11] since the transition state for the formation of *trans*-III would be expected to have lower energetic requirements as compared with the *cis* isomer.

trans-1-Chloro-2-(*p*-tolylmercapto)-ethene (III) was independently synthesized from acetylene and *p*-toluenesulfenyl chloride.[12–15] Such adducts have been assigned a *trans* structure,[12] and evidence presented in this paper, both chemical and infrared, verify this configurational assignment. Both intermediate III and authentic *trans*-III have characteristic infrared absorption bands at 8.44–8.46(m) μ and at 11.00–11.10(s) μ.[16] The infrared band at 7.78(s) μ characteristic for *cis*-III, which had been previously prepared by the stereospecific *trans* nucleophilic addition of sodium *p*-toluenethiolate to chloroacetylene,[2] was not found in the spectrum of intermediate III, nor in the spectrum of an authentic sample of *trans*-1-chloro-2-(*p*-tolylmercapto)-ethene. Furthermore, the sulfones of intermediate III and authentic *trans*-III did not show a melting point depression; both sulfones had characteristic infrared absorption bands at 8.46(m) and at 10.8(s) μ.

Additional evidence for such configurational assignments was offered by the comparative reactivities of intermediate III, authentic *trans*-III and *cis*-III in the base-catalyzed reactions with sodium *p*-toluenethiolate. Neither intermediate III nor authentic *trans*-III reacted with the arylthiolate in the absence of ethoxide; in the presence of the latter, up to 10.2% conversion to V was obtained under atmospheric reflux conditions. In contrast, *cis*-III gave a 98.3% conversion to V in the presence of ethoxide; in its absence, no reaction occurred.[2] By application of the rule of *trans* elimination[17–19] to these data, the configurational assignments previously made[12] are supported. Intermediate III (as well as authentic *trans*-III), however, do give V in considerably higher yield under more vigorous conditions (sealed tube at 85–100°; quantitative yield). Here, too, the conversion to V is diminished in the absence of sodium ethoxide (22.5% conversion).

The stereospecificity of the above reaction, *i.e.*, the conversion of a *trans* starting material III to an exclusively *cis* product V is of interest. Since it has been shown that the conversion of III to V is base catalyzed, then *p*-tolylmercaptoacetylene (IV) must be considered as an intermediate.[20] In other work, IV was independently synthesized and when treated with arylthiolate ion, gave V as a result of a stereospecific *trans* nucleophilic addition process.[2]

It has been suggested that the conversion of III to V might also proceed *via* an addition–elimination sequence, in a manner similar to the proposed path of I to intermediate III. However, such a path would not appear likely, since *trans*-V would be the expected product if the *cis* effect[11] could be applied to the base-catalyzed conversion of III to V.[21]


III

trans-V

trans-V has not been detected in any of the reactions of I, II or III with the arylthiolate. In one reaction compound I was converted to V, and the reaction mixture was fractionally crystallized to give 9 crops, each of which melted at the value for *cis*-V.

In view of the paucity of information on reactions of nucleophilic agents with vinylidene chloride (I), further investigations along those lines are being initiated.

Correlation of Infrared Spectral Data from Current Studies.—Lately, much interest has been shown in shifts in the infrared spectra of *cis*- and *trans*-olefins as a result of direct polar substitution or conjugation effects.[22–25] In our current studies,[2,3] a series of *cis*- and *trans*-olefins containing polar groups such as chlorine, sulfur or sulfone attached to the carbon–carbon double bond have been prepared and characterized. In Table I characteristic bands for various *cis* and *trans* isomeric systems are presented.

Within the *trans* series the in-plane bending bands of the ethylenic hydrogens show a consistent shift from the 7.55–7.85 μ region reported[26] for

TABLE I

CHARACTERISTIC BANDS FOR OLEFINS CONTAINING POLAR GROUPS

Compound	*cis*, μ	*trans*, μ
$(Cl)CH{=}CH(Cl)$[a]	7.83(s)	8.44(s), 11.25(s)
$(C_7H_7S)CH{=}CH(Cl)$	7.78(s)	8.44(m), 11.05(s)
$(C_7H_7SO_2)CH{=}CH(Cl)$	[b]	8.46(s), 10.82(s)
$(C_7H_7S)CH{=}CH(SC_7H_7)$	7.73(s)[c]	8.46(s), 10.88(s)
$(C_7H_7SO_2)CH{=}CH(SO_2C_7H_7)$	[b]	8.55(s), 10.62(s)

[a] Matheson, Coleman and Bell, redistilled: *cis*, b.p. 59.0° (737.0 mm.), $n^{20}\text{D}$ 1.4481; *trans*, b.p. 48.3–48.6° (742.5 mm.), $n^{20}\text{D}$ 1.4450. [b] The sulfone band at 7.41–7.69 μ[26] masks out the *cis* band; both compounds have characteristic bands at 14.65–14.68 μ. [c] Note that this was previously read erroneously as 7.48 μ, *cf.* ref. 3.

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[16] For tabulations of the infrared spectra of *cis*- and *trans*-olefins containing polar groups, see Table I.

[17] A. Michael, *J. prakt. Chem.*, **52**, 308 (1895); THIS JOURNAL, **40**, 1693 (1918).

[18] P. Pfeiffer, *Z. physik. Chem.*, **48**, 40 (1904).

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[20] In reference 2, chloroacetylene was treated with sodium *p*-toluenethiolate to give *cis*-III and V. The infrared spectrum of a forerun of III showed the characteristic absorption bands for a monosubstituted acetylene at 3.08 μ and for an acetylenic bond at 4.90 μ. These bands were also found in an authentic sample of *p*-tolylmercaptoacetylene (IV).

[21] *cis*-V has been thermally isomerized to the *trans* isomer by slow distillation.[8]

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trans-dialkyl olefins to the 8.44–8.55 μ region. Similar shifts have been reported for *trans*-1-bromo-1-propene (8.32 μ)[23] and *trans*-1-chloro-1-propene (8.13 μ)[23]. A similar shift has also occurred for the out-of-plane bending vibration of the ethylenic hydrogens for these *trans*-olefins from 10.20–10.35 μ[26] to 10.62–11.25 μ, the nature of the substituent controlling the extent of the shift. Such shifts have been observed for *trans*-1-bromo-1-propene (10.75 μ) and *trans*-1-chloro-1-propene (10.7 μ),[22,23,25] as well as for *trans*-1-halo-3,3,3-trifluoro-1-propenes (10.64–10.71 μ).[25]

For the *cis* series in the present study, a consistent shift is again found for the in-plane bending band of the olefinic hydrogens from 7.10–7.40 μ[26] to 7.73–7.78 μ (Table I). Such shifts have been reported for *cis*-1-chloro-1-propene (7.65 μ)[23] and *cis*-1-bromo-1-propene (7.78 μ).[23]

Experimental[27]

Vinylidene chloride[28] was distilled from its stabilizer through a short packed column (10 inches), and a constant-boiling fraction, b.p. 31.6° (748 mm.), was collected directly in a chilled Carius tube. Since polymerization problems had been experienced previously in sealed tube reactions involving vinylidene chloride and potassium sulfite in a water-ethylene glycol solvent system,[4] diphenylamine, a free radical inhibitor, was added to the reaction mixture. Furthermore, the Carius tube was flushed with nitrogen before and after addition of the reactants in order to minimize such polymerization difficulties.

Reaction of Vinylidene Chloride and Sodium *p*-Toluenethiolate. A. Preparation of V.—Vinylidene chloride (2.91 g., 2.39 ml., 0.03 mole), 7.45 g. (0.06 mole) of *p*-toluenethiol, 1.52 g. (0.066 mole) of sodium and 0.1 g. of diphenylamine in 45.0 ml. of absolute ethanol were heated in a sealed Carius tube at 110° for 65.5 hours. Sodium chloride (3.50 g.) was filtered off and washed with hot absolute ethanol. The filtrate was concentrated, diluted with water and extracted with petroleum ether (30–60°). The ethereal extracts were dried over magnesium sulfate, evaporated and crystallized from absolute ethanol to give 6.92 g. (84.7% conversion, 85.3% yield) of a solid, m.p. 91.0–91.5°, which did not depress the melting point of an authentic sample of *cis*-1,2-bis-(*p*-tolylmercapto)-ethene (V), m.p. 90.5–91.0°. A non-crystallizable oil, wt. 1.40 g., was also obtained but was not identified.

The remainder of the reaction mixture was acidified with concd. hydrochloric acid, extracted with petroleum ether and the extracts dried over magnesium sulfate and evaporated to give a solid, m.p. 39–40°, wt. 0.07 g., representing 0.94% recovery of *p*-toluenethiol.

B. Preparation of II.—A solution of 8.73 g. (0.09 mole) of vinylidene chloride, 7.45 g. (0.06 mole) of *p*-toluenethiol, 0.69 g. (0.03 mole) of sodium and 0.10 g. of diphenylamine in 45 ml. of absolute ethanol was heated in a sealed Carius tube at 50° for 24 hours. Sodium chloride (0.07 g.) was filtered off and washed with hot absolute ethanol. The filtrate was concentrated, diluted with water and extracted with petroleum ether. To remove any unreacted *p*-toluenethiol in the petroleum ether extracts, the latter was extracted with 25 ml. of 5 *N* potassium hydroxide, followed by washing with 25 ml. of water. The petroleum ether extracts were dried over magnesium sulfate and evaporated to give an oil, wt. 3.90 g., which distilled at 117.5–119.5° (2.3 mm.), n^{20}_D 1.5781 (3.80 g., 28.60% conversion or 59.40% yield of 1,1-dichloro-2-(*p*-tolylmercapto)-ethane (II)).

The sulfone of this liquid (0.50 g., 0.00226 mole) was prepared by oxidation with 5.0 ml. of 30% hydrogen peroxide in 30.0 ml. of glacial acetic acid; the product was recrystallized from 80% ethanol, m.p. 80.0–81.0° (wt. 0.59 g., 100% yield).

Anal.[29] Calcd. for $C_9H_{10}O_2Cl_2S$: C, 42.70; H, 3.98; Cl, 28.01. Found: C, 43.00; H, 4.29; Cl, 27.81.

The remainder of the reaction mixture was acidified with concd. hydrochloric acid, extracted with petroleum ether (30–60°), and the extracts were dried over magnesium sulfate and evaporated to a solid, m.p. 40.0–41.0° (3.85 g. or 51.6% recovery of *p*-toluenethiol).

The conversion of intermediate II to the final product V was effected by heating a solution of 0.50 g. (0.00226 mole) of 1,1-dichloro-2-(*p*-tolylmercapto)-ethane (II), 0.281 g. (0.00226 mole) of *p*-toluenethiol and 0.092 g. (0.0004 mole) of sodium in 40 ml. of absolute ethanol at 100° for 80.5 hours in a sealed tube. Sodium chloride (0.26 g.) was filtered off, the filtrate concentrated, diluted with water and extracted with petroleum ether (30–60°). These extracts were evaporated and crystallized from 95% ethanol to give 0.43 g. (69.8% conversion) of product melting at 91.0–92.0°. No depression was observed with an authentic sample of *cis*-1,2-bis-(*p*-tolylmercapto)-ethene (V), m.p. 91.0°. From the acidified reaction mixture, 0.10 g. (35.6%) of *p*-toluenethiol was recovered.

C. Isolation of Intermediate III.—A solution of 2.91 g. (0.03 mole) of vinylidene chloride, 7.45 g. (0.06 mole) of *p*-toluenethiol, 1.24 g. (0.054 mole) of sodium and 0.10 g. of diphenylamine in 45 ml. of absolute ethanol was heated in a sealed Carius tube at 65° for 49.5 hours. Sodium chloride (1.44 g.) was filtered off and washed with hot absolute ethanol. The filtrate was concentrated, diluted with water and extracted with petroleum ether (30–60°). The extracts were dried over magnesium sulfate, evaporated and crystallized from absolute ethanol. No solid product was isolated; instead, 5.70 g. of an oil was obtained. Distillation gave 1.76 g. (31.7% conversion) of a liquid, b.p. 125° (6.0 mm.), having an infrared spectrum identical with that of an authentic sample of *trans*-1-chloro-2-(*p*-tolylmercapto)-ethene, which had been prepared previously from acetylene and *p*-toluenesulfenyl chloride and had characteristic bands at 8.44–8.46 (m) μ and at 11.00–11.10 (s) μ. The infrared absorption bands and comparative intensities for independently synthesized III are (0.02 mm. or capillary film)[30]: 3.35(m), 3.49(w), 4.35(w), 5.30(w), 5.90(w), 6.28(w), 6.45(w), 6.72(s), 6.94(m), 7.17(m), 7.27(w), 7.68(w), 7.79(w), 7.90(w), 8.28(w), 8.44(m), 8.97(w), 9.18(m), 9.64(w), 9.84(m), 11.05(s), 12.00(s), 12.50(s) and 14.35(w) μ.

The sulfone of intermediate III (0.10 g., 0.0054 mole) was prepared in 94% yield (0.11 g.) with 2.0 ml. of 30% hydrogen peroxide in 20 ml. of glacial acetic acid, m.p. 45.5 46.5°, on recrystallization from 80% ethanol.

Anal. Calcd. for $C_9H_9ClO_2S$: C, 49.84; H, 4.19; Cl, 16.36. Found: C, 49.22; H, 4.23; Cl, 16.01.

This sulfone did not depress the melting point of an authentic sample of *trans*-1-chloro-2-(*p*-tolylsulfonyl)-ethene, m.p. 45.5–46.5°. The infrared spectra of these two sulfones had characteristic absorption bands at 8.46(m) μ and at 10.82(s) μ (carbon tetrachloride, 0.06 mm. thickness).

The remainder of the reaction mixture was acidified with concd. hydrochloric acid, extracted with petroleum ether (30–60°), the extracts were dried over magnesium sulfate and evaporated to give a solid, m.p. 40.0–42.0° (2.64 g., or 35.4% recovery of *p*-toluenethiol).

Under sealed tube conditions, III was treated with arylthiolate ion in the presence of sodium ethoxide to give a quantitative yield of V. Intermediate III (0.47 g., 0.00255 mole), 0.318 g. (0.00255 mole) of *p*-toluenethiol, 0.069 g. (0.003 mole) of sodium in 40 ml. of absolute ethanol were heated at 100° for 37.0 hours. Sodium chloride (0.19 g.) was filtered off and washed with hot absolute ethanol. The filtrate was concentrated, diluted with water, extracted with petroleum ether (30–60°), the extracts evaporated and crystallized from 95% ethanol to give 0.70 g. (100% yield) of *cis*-1,2-bis-(*p*-tolylmercapto)-ethene (V), m.p. 90.0–91.0°.

D. Isolation of III and V in the Same Reaction.—Even though intermediates II and III are the main products when mild conditions are employed, the presence of excess sodium ethoxide can cause further reaction to give V. Vinylidene chloride (2.91 g., 2.39 ml., 0.03 mole), 7.45 g. (0.06 mole) of *p*-toluenethiol, 1.52 g. (0.066 mole) of sodium, 0.10 g. of diphenylamine and 45.0 ml. of absolute ethanol were heated at 45° for 49 hours in a sealed tube. Sodium chloride (0.80

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(27) All boiling and melting points are uncorrected.

(28) We are indebted to the Dow Chemical Co. for a research grade sample of vinylidene chloride.

(29) The microanalyses were done by Dr. C. S. Yeh and Mrs. S. L. Margerum of the Purdue Chemistry Microanalytical Laboratory.

(30) The infrared spectra were run by Mrs. B. Polister and Mr. H. Susi of the Purdue Chemistry Infrared Laboratory with a Perkin-Elmer infrared spectrophotometer, model 21.

g.) was filtered off and washed with hot absolute ethanol. The filtrate was concentrated, diluted with water and extracted with petroleum ether (30–60°). The extracts were dried over magnesium sulfate, evaporated and recrystallized from absolute ethanol to give 0.70 g. (8.52% conversion to V), of product having m.p. 88–90°, and with no effect on the m.p. of an authentic sample of *cis*-1,2-bis-(*p*-tolylmercapto)-ethene (V), m.p. 90–91°. An oil, wt. 1.40 g., which could not be crystallized, was fractionally distilled, b.p. 84.0–86.0° (1.0 mm.) (wt. 0.89 g., 16.1% conversion to III). The infrared spectrum of this liquid was identical with that of an authentic sample of *trans*-1-chloro-2-(*p*-tolylmercapto)-ethene, which has characteristic absorption bands at 8.46(m) μ and 11.10(s) μ.

The sulfone of this liquid (0.20 g., 0.0108 mole) was prepared from 2.0 ml. of 30% hydrogen peroxide in 25.0 ml. of glacial acetic acid; wt. 0.20 g. (85.4% yield), m.p. 46.5–47.0° (from 80% ethanol). This sulfone did not depress the melting point of *trans*-1-chloro-2-(*p*-tolylsulfonyl)-ethene m.p. 45.0–46.5°. The infrared spectra of these two sulfones were identical (carbon tetrachloride, 0.06 mm. thickness).

The remainder of the reaction mixture was acidified with concd. hydrochloric acid, extracted with petroleum ether (30–60°), the extracts dried over magnesium sulfate and evaporated to give a solid, m.p. 40–42° (4.63 g., or 62.1% recovery of *p*-toluenethiol).

***trans*-1-Chloro-2-(*p*-tolylmercapto)-ethene.**—*p*-Toluenesulfenyl chloride was prepared by the chlorination of di-*p*-tolyl disulfide,[31,32] b.p. 91.0–93.0° (5.5 mm.), 86.4% yield [reported[31] 77.5–78.5° (2.5 mm.)]. The freshly distilled material was used immediately, if possible. Otherwise, *p*-toluenesulfenyl chloride was stored in a refrigerator with special precautions to exclude moisture and light.

Acetylene (Prest-O-Lite) was passed successively through towers containing water, sulfuric acid and soda-lime into a chilled flask (0°) containing 500 ml. of dried ethyl acetate. After one hour, 63.0 g. (0.397 mole) of *p*-toluenesulfenyl chloride in 200 ml. of ethyl acetate was added during a 2-hour period, while acetylene was still passed into the reaction mixture. At the end of this addition, acetylene was passed in for an additional hour. After standing for 12 hours at room temperature, the solvent was evaporated to give an oil (wt. 66.5 g.) which was fractionally distilled, b.p. 104.5–105.0° (4.0 mm.), $n^{20}\text{D}$ 1.5918 (24.5 g., 33.5% conversion to *trans*-1-chloro-2-(*p*-tolylmercapto)-ethene). Its infrared spectrum showed two characteristic bands at 8.44(m) μ and at 11.05(s) μ.

The sulfone of *trans*-1-chloro-2-(*p*-tolylmercapto)-ethene (1.0 g., 0.0054 mole) was prepared from 3.96 g. (7.6 ml.) of 30% hydrogen peroxide in 30 ml. of glacial acetic acid; wt. 0.93 g. (79.5% yield), m.p. 46.5–47.0° (from 80% ethanol).

Anal. Calcd. for $C_9H_9ClO_2S$: C, 49.84; H, 4.19; Cl, 16.36. Found: C, 50.01; H, 4.03; Cl, 16.35.

The infrared spectrum of this sulfone had characteristic absorption bands at 8.46(m) μ and 10.82(s) μ (carbon tetrachloride, 0.06 mm. thickness). Upon admixture with its *cis* isomer[2] (m.p. 38.0–39.0°), a viscous non-crystallizable liquid was obtained.

Further support for the *trans* configurational assignment to this adduct was obtained from two sets of experiments, one under atmospheric pressure conditions, the other, under sealed tube conditions.

Reaction of III with Thiolate Reagent. A. Atmospheric Pressure Conditions.—A solution of 1.0 g. (0.0054 mole) of *trans*-1-chloro-2-(*p*-tolylmercapto)-ethene, 0.672 g. (0.0054 mole) of *p*-toluenethiol, 0.138 g. (0.0060 mole) of sodium in 50 ml. of absolute ethanol was refluxed for 12 hours under a nitrogen atmosphere. Sodium chloride (0.01 g.) was filtered off and washed with hot absolute ethanol. The filtrate was concentrated, diluted with water, extracted with petroleum ether (30–60°), the extracts were evaporated and the residue was recrystallized from 95% ethanol to give 0.15 g. (10.2% conversion) of product melting at 90.0–90.5°. No depression occurred with an authentic sample of *cis*-1,2-bis-(*p*-tolylmercapto)-ethene (V), m.p. 91.0–91.5°. Unreacted *trans*-1-chloro-2-(*p*-tolylmercapto)-ethene (0.75 g., 75.0%) was recovered from the non-crystallizable alcoholic solution. From the acidified reaction mixture 0.60 g. (89.4%) of *p*-toluenethiol, m.p. 39.0–40.0°, was recovered.

The base-dependency of this reaction was demonstrated in an identical experiment which was run concurrently, except that no molar excess of sodium ethoxide (0.11 g., 0.00486 mole) to *p*-toluenethiol (0.672 g., 0.0054 mole) was used. No sodium chloride was isolated. Most of the unreacted *trans*-haloölefin (0.95 g., 95.0%) and *p*-toluenethiol (0.48 g., 71.7%) were recovered.

Similar observations were also obtained in comparative experiments with intermediate III and the arylthiolate under atmospheric pressure reflux conditions.

B. Sealed Tube Conditions.—*trans*-1-Chloro-2-(*p*-tolylmercapto)-ethene (1.0 g., 0.0054 mole), 0.672 g. (0.0054 mole) of *p*-toluenethiol and 0.138 g. (0.006 mole) of sodium in 40 ml. of absolute ethanol were heated to 85° for 50 hours in a sealed tube. Sodium chloride (0.29 g.) was filtered off and washed with hot absolute ethanol. The filtrate was concentrated, diluted with water and extracted with petroleum ether (30–60°). These extracts were evaporated and crystallized from 95% ethanol to give 1.30 g. (88.5% yield) of product melting at 91.0–91.5°; it did not depress the m.p. of an authentic sample of *cis*-1,2-bis-(*p*-tolylmercapto)-ethene (V). No *p*-toluenethiol was recovered from the acidified reaction mixture.

The base-dependency of this reaction was demonstrated in an experiment in which no excess sodium ethoxide was used and a slightly higher temperature was employed (100° for 50 hours): 1.0 g. (0.0054 mole) of *trans*-1-chloro-2-(*p*-tolylmercapto)-ethene, 0.672 g. (0.0054 mole) of *p*-toluenethiol, 0.11 g. (0.00486 mole) of sodium in 40 ml. of absolute ethanol. From the reaction mixture, 0.09 g. of sodium chloride, 0.33 g. (22.5% conversion) of *cis*-1,2-bis-(*p*-tolylmercapto)-ethene (V) (m.p. 90.5–91.0°) and 0.79 g. (79.0%) of the *trans*-haloölefin were isolated.

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