Nitration of Benzamide.—A solution of 10 g. (0.03 mole) of finely powdered benzamide in 55 ml. of sulfuric acid was stirred at 15°. To this was added 8.4 g. of potassium nitrate (0.03 mole). The mixture was stirred at room temperature for 3 hr. The product isolated by pouring the mixture onto 400 g. of ice weighed 12.3 g. (89%) and melted at 143° (3-nitrobenzamide, m.p. 143°).[18,35] Basic hydrolysis followed by acidification produced an acid melting at 140° (3-nitrobenzoic acid, m.p. 140°).[30] A mixture melting point with an authentic sample of 3-nitrobenzoic acid was not lowered.

B.—To 35 ml. of fuming nitric acid (Sp. Gr. 1.49) decolorized with urea, was added 10 g. of finely powdered benzamide. Fuming sulfuric acid (17 ml.) was added slowly with stirring at 0°. The mixture was stirred for 10 min. and poured onto ice. There was isolated 12.6 g. (92%) of product melting at 143°. A mixture melting point with an authentic sample of 3-nitrobenzamide was not lowered. Substitution of concentrated sulfuric acid for fuming sulfuric acid resulted in the recovery of unaltered benzamide [9.7 g. (98%), m.p. 126°]. A mixture melting point with an authentic sample of benzamide was not lowered.

C.—The product obtained by allowing 10 g. of benzamide to react with a fuming nitric acid–acetic anhydride mixture for 10 hr. at 0° weighed 9.4 g. (93%) and melted at 120° (benzoic acid, m.p. 121°).[22] A mixture melting point with an authentic sample of benzoic acid was not lowered. When the reaction time was reduced to 15 min., 9.1 g. (90%) of benzoic acid was obtained.

D.—Benzamide was treated with an acetic anhydride-cupric nitrate trihydrate mixture for 2 hr. at 0°; the product isolated weighed 8.8 g. (87%) and melted at 119°. A mixture melting point with benzoic acid was not lowered. When the reaction was allowed to proceed for only 5 min. two products were isolated: (1) benzamide, 2.8 g. (28%), m.p. 127°; and (2) benzoic acid, 5.1 g. (57%), m.p. 122°.

Nitration of 3-Nitrobenzamide.—Treatment of 10 g. of 3-nitrobenzamide with fuming nitric acid–fuming sulfuric acid as before yielded 9 g. of unaltered starting material, identified by mixture melting point.

Measurement of Spectra.—The ultraviolet measurements were made on a Cary Model 11 recording spectrophotometer from 4000–2400 Å. Samples were run in isooctane at molar concentrations of 1×10^{-4} and 1×10^{-5} in a 1-cm. silica cell with matched blank solvent cell. Representative spectra are listed on Table III.

The Perkin-Elmer Model 21 double-beam spectrophotometer was used to obtain the infrared data. The spectra were run in carbon tetrachloride at a concentration of 15 mg./ml. in 0.1-mm. sodium chloride cells (see Table IV).

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[35] E. Reid, *Am. Chem. J.*, **21**, 290 (1899).

The Products of the Reactions of Sodium *t*-Butylmercaptide with Vinyl Chloride, Vinylidene Chloride, and *cis*- and *trans*-Dichloroethylenes[1,2]

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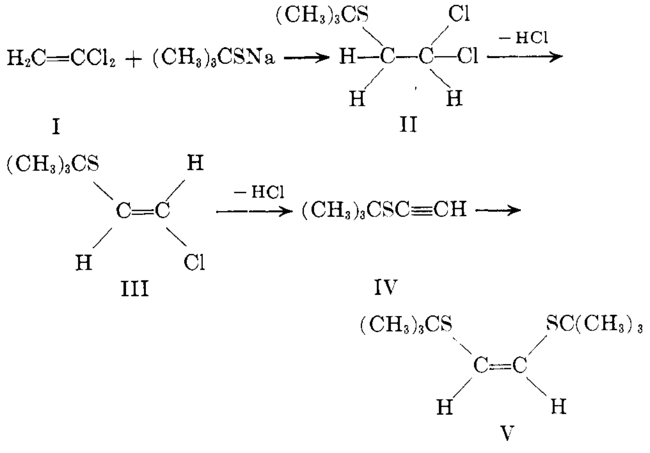
The products of the reactions of alcoholic sodium *t*-butylmercaptide with vinyl chloride, vinylidene chloride, and *cis*- and *trans*-dichloroethylenes are described.

Previous work in this laboratory on nucleophilic reactions of *p*-toluenethiolate[2] and *p*-tolueneselenolate[3] reagents with haloethylenes has been extended to an aliphatic thiolate,[4] sodium *t*-butylmercaptide. The major reaction paths were found to be the same as those observed with *p*-toluenethiolate and *p*-tolueneselenolate,[4] *i.e.*, elimination–addition with vinyl chloride and *cis*- and *trans*-dichloroethylene, and addition-elimination with vinylidene chloride. One difference resulted from the greater basicity of sodium *t*-butylmercaptide. Whereas, in the reaction of *cis*-dichloroethylene with *p*-toluenethiolate, excess sodium ethoxide is required for initial dehydrohalogenation, sodium *t*-butylmercaptide is sufficiently basic to effect initial dehydrohalogenation.

Vinyl Chloride.—Vinyl chloride reacts with sodium *t*-butylmercaptide in the presence of sodium ethoxide at elevated temperatures to give *t*-butylmercaptoethene, presumably by the elimination–addition sequence observed with aromatic thiolates.[2]

$$CH_2{=}CHCl + (CH_3)_3CSNa \xrightarrow[\Delta]{EtONa} HC{\equiv}CH \longrightarrow (CH_3)_3CSCH{=}CH_2$$

Vinylidene Chloride.—By analogy to the reaction with sodium *p*-toluenethiolate, it would be predicted that the first step in the reaction of sodium *t*-butylmercaptide with vinylidene chloride should be addition followed by elimination. In fact vinylidene chloride is comparatively resistant to dehydrohalogenation.[2] In further agreement with this hypothesis is the isolation of 1,1-dichloro-2-(*t*-butylmercapto)ethane (II) together with *trans*-1-chloro-2-(*t*-butylmercapto)ethene (III) from the reaction of vinylidene chloride with sodium *t*-butylmercaptide at 50°.



When vinylidene chloride is treated with sodium *t*-butylmercaptide at 100°, *trans*-1-chloro-2-(*t*-butylmercapto)ethene (III) and *cis*-1,2-bis(*t*-butylmercapto)ethene (V) are isolated from the reaction mixture.

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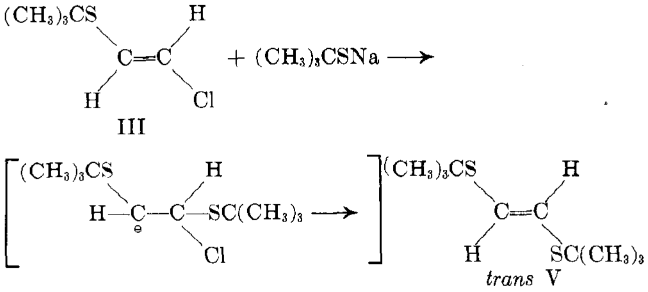
[1] For preceding paper see W. E. Truce and B. Groten, *J. Org. Chem.*, **27**, 128 (1962).

[2] Nucleophilic replacements from olefinic carbons have been summarized by several authors, *e.g.*, N. Kharasch, "Organic Sulfur Compounds," Ed., W. E. Truce, Chap. 12, Pergamon Press, New York, N. Y., 1961; Abstracts, 17th National Organic Chemistry Symposium of the American Chemical Society, 1961.

[3] G. R. Price, Ph.D. thesis, Purdue University, Lafayette, Ind. (1959).

[4] Some over-all reactions of aliphatic thiolates with a few vinylic halides and thioacetylenes have been studied previously, J. F. Arens, *Advan. Org. Chem.*, **2**, 117 (1960).

With longer reaction times at 100°, *cis*-1,2-bis(*t*-butylmercapto)ethene (V) is the only product isolated. Intermediate III is recovered unchanged by treatment with sodium *t*-butylmercaptide in refluxing alcohol but is converted to V by treatment with sodium *t*-butylmercaptide at 100°. The conditions necessary for the conversion of intermediate III to V and the configuration of the final product (V) suggest an elimination–addition sequence. An incipient carbanion step would favor, by virtue of the *cis* effect[5] and by analogy to systems where it is known to occur,[2] a *trans* configuration for the final product; however, *trans* V was not isolated.

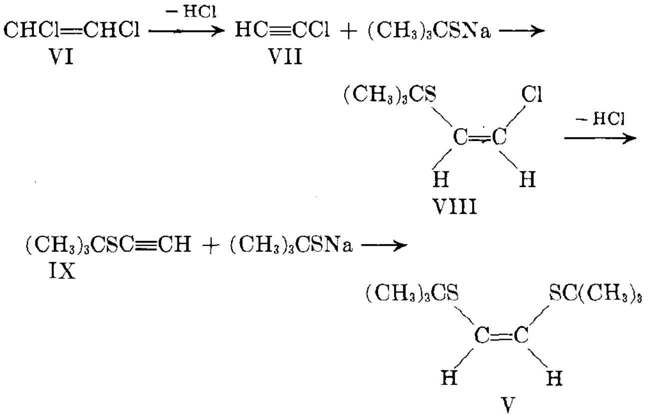


Intermediate II was identified by elemental analysis of its corresponding sulfone and by conversion to III with sodium ethoxide. Intermediate III was identified by elemental analysis of its corresponding sulfone. The *trans* configuration was assigned on the basis of the infrared spectra of the sulfide and sulfone. The absorption spectrum of the sulfide contained a strong band at 10.97 μ, while that of the sulfone contained one at 10.57 μ. These bands are characteristic of the *trans* configuration for this type of compound[1] and were absent in the isomeric sulfide (and its sulfone), which was prepared by the reaction of chloroacetylene with sodium *t*-butylmercaptide and was assigned the *cis* configuration. The *cis* structure of the final product (V) was assigned on the basis of its infrared spectrum. The absorption spectrum of this product contained a strong peak at 7.70 μ, which is characteristic of a *cis* structure for this type of compound.[1] A mixture melting point with the product from the reaction of *cis*-dichloroethylene with sodium *t*-butylmercaptide showed no depression.

***cis*- and *trans*-Dichloroethylene.**—On the basis of the results obtained with sodium *p*-toluenethiolate, the first step in the reaction of sodium *t*-butylmercaptide with *cis*-dichloroethylene should be elimination to form chloroacetylene followed by addition of the elements of *t*-butylmercaptan.

Facile dehydrohalogenation of *cis*-dichloroethylene has been demonstrated by several different workers.[6] In contrast to the reaction of *cis*-dichloroethylene with *p*-toluenethiolate, where there is practically no reaction in the absence of ethoxide, reaction with *t*-butylmercaptide occurs in the absence of ethoxide ion, but at a slower rate. This reaction of sodium *t*-butylmercaptide with *cis*-dichloroethylene is due to dehydrohalogenation by the sodium *t*-butylmercaptide itself. The relative pK_a values[7] of *p*-toluenethiol (8.3), phenol (9.85), and *t*-butylmercaptan (12.7) show that sodium *t*-butylmercaptide is an appreciably stronger base than sodium *p*-toluenethiolate. When *cis*-dichloroethylene is treated with sodium *p*-toluenethiolate in the presence of sodium phenoxide, which is a weaker base than sodium *t*-butylmercaptide, reaction takes place although at a slower rate than in the presence of sodium ethoxide.

That dehydrohalogenation is an initial step also is supported by the inactivity of *trans*-dichloroethylene with sodium *t*-butylmercaptide under refluxing alcohol conditions. The intermediacy of chloroacetylene (VII) was demonstrated further by generating chloroacetylene according to the method of Ott[8] and treating it with sodium *t*-butylmercaptide, whereby *cis*-1-chloro-2-(*t*-butylmercapto)ethene was produced. Treatment of this intermediate (VIII) with potassium hydroxide readily gave *t*-butylmercaptoacetylene (IX). The addition of sodium *t*-butylmercaptide to *t*-butylmercaptoacetylene occurs readily to give the final product *cis*-1,2-bis(*t*-butylmercapto)ethene (V).



Intermediate VIII was identified by elemental analysis of its corresponding sulfone. The *cis* configuration was assigned on the basis of the infrared spectra of the sulfide and sulfone. The absorption spectrum of the sulfide contained a strong peak at 7.80 μ, which is characteristic of the *cis*- configuration of this type of compound.[1] Both the sulfide and sulfone showed the absence of *trans* absorption peaks at 11.00 and 10.57 μ, respectively. The infrared spectrum of *t*-butylmercaptoacetylene (IX) showed the absorption at 3.10 and 4.95 μ, which are characteristic of a terminal acetylene. The final product (V) was assigned the *cis* configuration on the basis of its infrared spectrum, which showed a strong absorption peak at 7.70 μ. The *trans* isomer, which was prepared by partial isomerization of the *cis* product with heat, showed an absorption peak at 10.75 μ. These absorption peaks are characteristic of *cis* and *trans* structures, respectively, for this type of compound.[1]

Oxidation of *trans* V with peracetic acid gave the *trans*-sulfone, which crystallized from the oxidation mixture and melted without decomposition. Attempts to oxidize *cis* V with peracetic acid were unsuccessful; however, when the sulfone of *cis* V was prepared by oxidation with perbenzoic acid it melted with decomposition. Construction of the model of *cis*-1,2-bis(*t*-butylsulfonyl)ethene shows considerable strain within the molecule.

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(5) D. Y. Curtin, *Record of Chem. Progr. (Kresge-Hooker Sci. Lib.)*, **15**, 111 (1954); Abstracts, 13th National Organic Chemistry Symposium of the American Chemical Society, 1953.

(6) S. I. Miller and R. M. Noyes, *J. Am. Chem. Soc.*, **74**, 629 (1952).

(7) Jean Maurin and Rene A. Paris, *Compt. rend.*, **232**, 2428 (1951).

(8) E. Ott, *Ber.*, **76**, 87 (1943).

When *trans*-dichloroethylene was treated with sodium *t*-butylmercaptide at 130° a liquid product was obtained in contrast to the solid product, *cis*-1,2-bis(*t*-butylmercapto)ethene (V), m.p. 58°, obtained from *cis*-dichloroethylene. The liquid product was identified as a mixture of *cis* and *trans* V. The infrared spectrum of this liquid was identical with that of *cis*-1,2-bis(*t*-butylmercapto)ethene indicating that the amount of *trans* isomer was less than 5%. By freezing from a petroleum ether solution pure *cis*-1,2-bis(*t*-butylmercapto)ethene could be obtained. When this mixture of isomers (11 g.) was oxidized with excess peracetic acid, 0.5 g. of the *trans* sulfone was obtained indicating approximately 5% of the *trans* isomer in the original mixture.

Since at elevated temperatures in the presence of strong base, *trans*-dichloroethylene readily dehydrohalogenates to form chloroacetylene,[6] it is felt that the formation of *cis*-1,2-bis(*t*-butylmercapto)ethene from *trans*-dichloroethylene by treatment with sodium *t*-butylmercaptide proceeds by an elimination–addition sequence. The slow step in the reaction of *trans*-dichloroethylene appears to be initial dehydrohalogenation. It has been shown that *trans*-dichloroethylene could not be isomerized to *cis*-dichloroethylene under the reaction conditions,[2] therefore, ruling out isomerization as the first step in the reaction sequence.

Nuclear magnetic resonance studies provided additional support for structural assignments. The spin-spin coupling constants for *cis* and *trans* isomers in olefins have been found to be 6–14 and 11–18 c.p.s., respectively.[9] For compounds VIII and III, the spin-spin coupling constants were found to be 7 and 13 c.p.s., respectively.

Experimental[10]

Reaction of Vinyl Chloride with Sodium *t*-Butylmercaptide.—To 4.0 g. (0.065 mole) of vinyl chloride condensed into a Carius tube was added a sodium *t*-butylmercaptide solution prepared by dissolving 1.61 g. (0.0700) g.-atom) of sodium in 40 ml. of absolute ethanol and adding 5.8 g. (0.065 mole) of *t*-butylmercaptan. To the reaction mixture was added 0.1 g. of diphenylamine as a free radical inhibitor before flushing the tube with nitrogen and sealing. The tube was heated for 48 hr. at 130°. The tube was then cooled and opened using a heated glass rod. The sodium chloride was filtered off, washed with hot absolute ethanol, dried, and weighed (wt. of sodium chloride, 1.9 g.). The filtrate was diluted with water and extracted several times with petroleum ether (35–37°). The combined extracts were dried over magnesium sulfate and the petroleum ether evaporated. The liquid which remained was distilled to give 1.25 g. (0.0108 mole, conversion 17%) of *t*-butylmercaptoethane, b.p. 114°, $n^{20}\mathrm{D}$ 1.4615; lit.[11] b.p. 117–118°, $n^{20}\mathrm{D}$ 1.4622.

Reaction of Vinylidene Chloride with Sodium *t*-Butylmercaptide (Preparation of V).—The vinylidene chloride used was distilled through a short helix-packed column to separate it from its stabilizer and a constant boiling fraction, b.p. 31°, was collected.

To a sodium ethoxide solution prepared by dissolving 2.53 g. (0.110 g.-atom) of sodium in 40 ml. of absolute ethanol was added 9.0 g. (0.10 mole) of *t*-butylmercaptan. This mixture was placed in a Carius tube along with 4.8 g. (0.050 mole) of vinylidene chloride in which was dissolved 0.2 g. of diphenylamine. The contents of the tube were flushed with dry nitrogen, and the tube sealed. After heating to 110° for 65 hr. the contents of the tube was filtered to yield 4.6 g. of sodium chloride. The filtrate was diluted with water and the oil which formed extracted with ether. The ether extracts were combined and dried with anhydrous magnesium sulfate. The ether was evaporated and the residue distilled under reduced pressure to yield 5.8 g. (0.028 mole) of *cis*-1,2-bis(*t*-butylmercapto)ethene, b.p. 120–122° (10 mm.), m.p. 58–59°, on recrystallization from ethanol; lit.[12] m.p. 56–57°. A mixture melting point determination with the product from the reaction of dichloroethylene and sodium *t*-butylmercaptide showed no depression.

Reaction of Vinylidene Chloride with Sodium *t*-Butylmercaptide (Isolation of Intermediates II and III.)—To a sodium ethoxide solution prepared by dissolving 3.45 g. (0.150 g.-atom) of sodium in 40 ml. of absolute ethanol was added 18 g. (0.20 mole) of *t*-butylmercaptan. This mixture was placed in a Carius tube along with 9.7 g. (0.10 mole) of vinylidene chloride in which 0.2 g. of diphenylamine was dissolved. The contents were flushed with dry nitrogen and the tube sealed. After heating at 50° for 48 hr. the contents of the tube were filtered to yield 4.47 g. of sodium chloride. The filtrate was diluted with water and the oil formed extracted with ether. The ether extracts were combined and dried with anhydrous magnesium sulfate. The ether was evaporated and the residue distilled under reduced pressure to yield 2.3 g. (0.012 mole) of 1,1-dichloro-2-(*t*-butylmercapto)ethane, b.p. 76° (10 mm.), $n^{20}\mathrm{D}$ 1.4930, and 1.2 g. (0.008 mole) of *trans*-1-chloro-2-(*t*-butylmercapto)ethene, b.p. 71°(40 mm.), $n^{20}\mathrm{D}$ 1.4900.

The sulfone of 1,1-dichloro-2-(*t*-butylmercapto)ethane was prepared by oxidation with perbenzoic acid.[13]

1,1-Dichloro-2-(*t*-butylmercapto)ethane (1.0 g., 0.0053 mole) was dissolved in 20 ml. of chloroform and 200 ml. of a chloroform solution of perbenzoic acid (0.050 mole) added. The solution was allowed to stand at 0° for 12 hr. and at room temperature for 2 days. The solution was then treated with aqueous potassium bicarbonate and dried with magnesium sulfate. The chloroform was evaporated and the resulting residue recrystallized from water, m.p. 108°.

Anal. Calcd. for $C_6H_{12}SO_2Cl_2$: C, 32.90; H, 5.58. Found: C, 32.94; H, 5.50.

The sulfone of *trans*-1-chloro-2-(*t*-butylmercapto)ethene was prepared by oxidation with peracetic acid. *trans*-1-Chloro-2-(*t*-butylmercapto)ethene (1.0 g., 0.0060 mole) was dissolved in 20 ml. of acetic acid and 4 ml. (0.035 mole) of 30% hydrogen peroxide was added. The mixture was allowed to stand at room temperature for 2 days and then poured onto ice. The sulfone did not crystallize until seeded with a crystal of *trans*-1-chloro-2-(*t*-butylsulfonyl)ethene which had been prepared by oxidation with perbenzoic acid. Recrystallization from petroleum ether (b.p. 35–37°) gave a product which melted at 59–60°.

Anal. Calcd. for $C_6H_{11}SO_2Cl$: C, 39.56; H, 6.05. Found: C, 39.59; H, 6.20.

The infrared spectrum of *trans*-1-chloro-2-(*t*-butylmercapto)ethene showed peaks at following wave lengths: 3.30 (w), 3.45 (s), 6.00 (w), 6.25 (w), 6.43 (s), 6.85 (s), 7.15 (w), 7.30 (s), 7.75 (w), 7.85 (w), 8.50 (s, broad), 9.75 (w), **10.97** (s), 12.00 (s), 12.50 (s, broad), 14.00 (w), 15.10 (w) μ. The infrared spectrum of *trans*-1- chloro-2-(*t*-butylsulfonyl)ethene showed peaks at following wave lengths (Nujol mull): 3.30 (m), 3.40 (m), 3.50 (m), 5.75 (w), 5.90 (w), 6.30 (s), 6.80 (s), 7.15 (w), 7.20 (m), 7.95 (s), 8.40 (s), 8.95 (s), 9.75 (w), **10.57** (s), 11.85 (s), 12.10 (m), 12.57 (m) μ.

Reaction of Vinylidene Chloride with Sodium *t*-Butylmercaptide (Isolation of Intermediate III and V).—To a sodium ethoxide solution prepared by dissolving 2.53 g. (0.110 mole) of sodium in 40 ml. of absolute ethanol was added 9.0 g. (0.10 mole) of *t*-butylmercaptan. This mixture was placed in a Carius tube along with 4.8 g. (0.050 mole) of vinylidene chloride in which was dissolved 0.2 g. of diphenylamine. The contents of the tube were flushed with dry nitrogen and the tube sealed. After heating to 100° for 48 hr., the contents of the tube were filtered to remove the sodium chloride and the filtrate was diluted with water. The oil which formed was extracted with ether, and the ether extracts dried with anhydrous magnesium sulfate. The ether was evaporated and the residue distilled under reduced pressure to yield 0.80 g. (0.0053 mole) of *trans*-1-chloro-2-(*t*-butylmercapto)ethene, b.p. 71° (40 mm.) and 4.5 g. (0.022 mole) of *cis*-1,2-bis(*t*-butylmercapto)ethene, b.p. 120–122° (10 mm.), m.p. 59°, after recrystallization from ethanol.

Preparation of *trans*-1-Chloro-2-(*t*-butylmercapto)ethene from 1,1-Dichloro-2-(*t*-butylmercapto)ethane.—To a sodium ethoxide

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[9] L. M. Jackman, "Application of N.m.r. Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, p. 85.

[10] All melting and boiling points are uncorrected.

[11] J. F. Arens and T. Doornbos, *Rec. trav. chim.*, **75**, 481 (1956).

[12] H. J. Backer and J. Strating, *ibid.*, **73**, 565 (1954).

[13] "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 431.

solution prepared by dissolving 0.25 g. (0.011 g.-atom) of sodium in 25 ml. of absolute ethanol was added 2.0 g. (0.011 mole) of 1,1-dichloro-2-(*t*-butylmercapto)ethane. The solution was heated to reflux under a nitrogen atmosphere for 30 min. The mixture was cooled and the sodium chloride which had formed was filtered off. The filtrate was diluted with water and extracted with ether. The ether extracts were then dried with magnesium sulfate and the ether solvent evaporated. Vacuum distillation of the resulting residue gave 1.1 g. (0.0073 mole) of *trans*-1-chloro-2-(*t*-butylmercapto)ethene, b.p. 73°(40 mm.).

Attempted Reaction of *trans*-1-Chloro-2-(*t*-butylmercapto)ethene with Sodium *t*-Butylmercaptide.—To a sodium ethoxide solution prepared by dissolving 0.46 g. (0.020 g.-atom) of sodium in 50 ml. of ethanol was added 1.35 g. (0.0150 mole) of *t*-butylmercaptan. The solution was heated to reflux under a nitrogen atmosphere, and 2.0 g. (0.013 mole) of *trans*-1-chloro-2-(*t*-butylmercapto)ethene added dropwise. At the end of 6 hr. refluxing only a trace of sodium chloride had formed. The solution was cooled, diluted with water, and extracted with ether. The ether extracts were dried with anhydrous magnesium sulfate and the ether solvent evaporated. The residue was vacuum distilled and 1.4 g. of *trans*-1-chloro-2-(*t*-butylmercapto)ethene, b.p. 71° (40 mm.), recovered.

Attempted Synthesis of *trans*-1-Chloro-2-(*t*-butylmercapto)ethene from *t*-Butylsulfenyl Chloride and Acetylene.—*t*-Butylsulfenyl chloride was prepared by chlorination of *t*-butyl disulfide.[14] *t*-Butyl disulfide (45 g., 0.25 mole) was dissolved in 500 ml. of *n*-heptane. The solution was placed in a three-neck flask equipped with a stirrer, reflux condenser, and a chlorine inlet bubbler. Chlorine (14.2 g., 0.20 mole) was liquified and weighed. The solution was heated to reflux and the chlorine added as rapidly as possible through the gas inlet tube. After all the chlorine had been added, the solution was cooled to 0°. Because *t*-butylsulfenyl chloride decomposes on distillation[14,15] the *n*-heptane solution was added to an ice-cold ethyl acetate solution of acetylene.

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 dry ethyl acetate. After 1 hr., the *n*-heptane solution of *t*-butylsulfenyl chloride was added dropwise during a 2-hr. period. Acetylene was passed into the solution for an additional hour, and then the solution was allowed to stand at room temperature for 12 hr. The ethyl acetate and *n*-heptane solvents were distilled and the residue distilled under reduced pressure. Only *t*-butyl disulfide, b.p. 60° (5 mm.), and higher boiling fractions were isolated. No *trans*-1-chloro-2-(*t*-butylmercapto)ethene, b.p. 71° (40 mm.), was isolated.

A second attempt using *n*-heptane as a solvent for the acetylene gave the same results.

A third attempt using carbon tetrachloride as a solvent and aluminum chloride catalyst gave the same results.

To show that *t*-butylsulfenyl chloride was formed in the reaction of *t*-butyl disulfide with chlorine, a 20-ml. sample of the *n*-heptane solution of *t*-butylsulfenyl chloride was treated with 2 g. of piperazine. The solid which formed was recrystallized twice from ethanol to give *t*-butylsulfenyl piperazide, m.p. 119°, lit.[16] m.p. 120°.

Anal. Calcd. for $C_{12}H_{26}N_2S_2$: C, 54.96; H, 9.92. Found: C, 54.90; H, 10.08.

Reaction of *cis*-Dichloroethylene with the Sodium *t*-Butylmercaptide.—To a sodium ethoxide solution, prepared by dissolving 16 g. (0.70 g.-atom) of sodium in 260 ml. of absolute ethanol, was added 60 g. (0.66 mole) of *t*-butylmercaptan. The solution was heated to reflux with stirring under a nitrogen atmosphere. *cis*-Dichloroethylene (32 g., 0.33 mole) was added dropwise over the period of 1 hr., and the mixture was refluxed for an additional 6 hr. The mixture was cooled and poured into water. The oil which separated was extracted with diethyl ether, and the extracts dried over anhydrous magnesium sulfate. The ether was evaporated and the residue distilled under reduced pressure to yield 40 g. (0.20 mole) of *cis*-1,2-*bis*-(*t*-butylmercapto)ethene. Recrystallization from ethanol gave a product which melted at 59–60°, lit.[12] m.p. 56–57°.

Anal. Calcd. for $C_{10}H_{20}S_2$: C, 58.82; H, 9.40. Found: C, 59.09; H, 9.90.

The infrared spectrum of *cis*-1,2-bis(*t*-butylmercapto)ethene showed peaks at the following wave lengths (Nujol mull): 3.35 (s), 3.53 (s), 6.50 (m), 6.90 (s), 7.33 (s), 7.70 (m), 8.25 (m), 8.60 (s), 9.75 (w), 10.70 (w), 11.20 (w), 12.10 (s), 13.90 (m), 14.63 (m, broad) μ.

The sulfone was prepared by treating 2.0 g. (0.10 mole) of the sulfide with 300 ml. (0.75 mole) of a chloroform solution of perbenzoic acid.[13] The solution was allowed to stand for 3 hr. at 0° and 48 hr. at room temperature. The chloroform solution was then treated with an aqueous solution of potassium bicarbonate and dried with anhydrous magnesium sulfate. The chloroform was evaporated and the solid which remained was recrystallized from acetic acid, m.p. 233° dec. Recrystallization a second time from ethanol gave a melting point of 242° dec., lit.[12] m.p. 235° dec.

Anal. Calcd. for $C_{10}H_{20}O_4S_2$: C, 44.77; H, 7.69. Found: C, 45.21; H, 8.00.

Attempts to prepare the sulfone of *cis*-1,2-bis(*t*-butylmercapto)ethene by oxidation with peracetic acid were unsuccessful.

Comparison of the Base Dependency of the Reactions of Sodium *t*-Butylmercaptide and Sodium *p*-Toluenethiolate with *cis*-Dichloroethylene.—Sodium (2.3 g., 0.10 g.-atom) was dissolved in 200 ml. of absolute ethanol and 18.0 g. (0.200 mole) of *t*-butylmercaptan was added. The solution was heated to reflux under a nitrogen atmosphere. *cis*-Dichloroethylene (9.7 g., 0.10 mole) was added dropwise and the mixture refluxed for 65 hr. The mixture was then cooled and the sodium chloride filtered off, washed with hot absolute ethanol, dried, and weighed (wt. of sodium chloride, 5.2 g., 89% reaction).

The same experimental procedure was followed using *p*-toluenethiol in place of *t*-butylmercaptan. No sodium chloride had formed at the end of 65 hr.

Reaction of Sodium *p*-Toluenethiolate with *cis*-Dichloroethylene in the Presence of Sodium Phenoxide.—Sodium (4.0 g., 0.18 g.-atom), *p*-toluenethiol (12.4 g., 0.100 mole), and phenol (9.4 g., 0.10 mole) were dissolved in 200 ml. of absolute ethanol and the solution heated to reflux under a nitrogen atmosphere. *cis*-Dichloroethylene (9.7 g., 0.10 mole) was added dropwise, and the mixture refluxed for 72 hr. The mixture was then cooled and the sodium chloride filtered off, washed with hot absolute ethanol, and weighed (wt. of sodium chloride, 4.9 g., 49% reaction).

Isomerization of *cis*-1,2-Bis-(*t*-butylmercapto)ethene.—*cis*-1,2-Bis-(*t*-butylmercapto)ethene (40 g., 0.20 mole) was dissolved in 50 ml. of absolute ethanol and the solution heated in a sealed Carius tube for 4 days at 130°. The Carius tube was cooled and opened. The ethanol was evaporated and the residue vacuum distilled through a short Vigreux column. A liquid fraction, 6.0 g., b.p. 112–122° (10 mm.), was collected before the recovered *cis*-1,2-bis(*t*-butylmercapto)ethene began to solidify in the condenser on cooling. This liquid fraction was then redistilled through a spinning band column. Two grams of liquid, b.p. 102° (5 mm.), n^{23}D 1.5140, was collected. Since temperature then rose to 108° (5 mm.) and recovered *cis*-1,2-bis(*t*-butylmercapto)ethene began to solidify in the condenser, the distillation was stopped.

The infrared spectrum of *trans*-1,2-bis(*t*-butylmercapto)ethene showed peaks at the following wave lengths: 3.42 (s), 6.25 (w), 6.50 (w), 6.77 (s), 7.15 (m), 7.30 (s), 7.65 (w), 8.20 (m), 8.55 (s, broad), 9.75 (w), 10.75 (s), 11.70 (m), 12.03 (s), 12.40 (s), 12.75 (m), 14.50 (w, broad) μ.

The corresponding sulfone was prepared by oxidation with peracetic acid. *trans*-1,2-Bis(*t*-butylmercapto)ethene (0.80 g., 0.0039 mole) was dissolved in 20 ml. of acetic acid and treated with 4 ml. (0.035 mole) of 30% hydrogen peroxide. The solution was allowed to stand for 2 days at room temperature. The crystalline sulfone which formed was filtered off and the filtrate poured onto ice–water to recover additional sulfone. The sulfone (0.73 g., 0.0031 mole) was recrystallized twice from ethanol, m.p. 228°.

Anal. Calcd. for $C_{10}H_{20}S_2O_4$: C, 44.77; H, 7.69. Found: C, 44.66; H, 8.00.

Various attempts to prepare the sulfone of *cis*-1,2-bis(*t*-butylmercapto)ethene by oxidation with peracetic acid were unsuccessful. Construction of the model of this sulfone shows it to be a very sterically hindered molecule.

Attempted Reaction of *trans*-Dichloroethylene with the Sodium *t*-Butylmercaptide Reagent.—Sodium (5.75 g., 0.250 g.-atom) was dissolved in 200 ml. of absolute ethanol and 18 g. (0.20 mole) of *t*-butylmercaptan was added. The solution was heated to reflux under a nitrogen atmosphere and 9.6 g. (0.10 mole) of *trans*-dichloroethylene was added dropwise. The mixture was allowed

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[14] W. A. Schulze, Phillips Petroleum Company, Bartlesville, Okla., private communication.

[15] H. Rheinboldt and F. Mott, *Ber.*, **72**, 668 (1939).

[16] H. Rheinboldt and E. Motzkus, *ibid.*, **72**, 657 (1939).

to reflux for 24 hr. The sodium chloride formed was filtered off, washed with hot absolute alcohol, dried, and weighed (wt. of sodium chloride, 0.77 g., 5% reaction).

Reaction of *trans*-Dichloroethylene with the Sodium *t*-Butylmercaptide Reagent.—To a sodium ethoxide solution prepared from 5.1 g. of sodium (0.22 g.-atom) in 40 ml. of ethanol was added 18.0 g. (0.200 mole) of *t*-butylmercaptan. The mixture was placed in a Carius tube along with 9.7 g. (0.10 mole) of *trans*-dichloroethylene. The tube and its contents were flushed with nitrogen, sealed, and placed in a tube furnace for 48 hr. at 130°. The Carius tube was then cooled, opened, and the sodium chloride (9.2 g.) filtered off, washed with hot absolute ethanol, dried, and weighed. The filtrate from the reaction mixture was concentrated by evaporation of the ethanol. Water was added and the oil which formed extracted with ether. The ether extracts were combined, dried with magnesium sulfate, and the ether evaporated. Vacuum distillation of the residue gave a liquid, 11.3 g., which distilled at 112–122° (10 mm.). The major part of the product distilled at 122° (10 mm.) and solidified in the condenser.

In order to determine the isomeric distribution of this mixture, the mixture was oxidized with peracetic acid. The mixture of isomers (11.3 g., 0.055 mole) was dissolved in 80 ml. of acetic acid and 40 ml. (0.35 mole) of hydrogen peroxide added. The oxidation mixture was allowed to stand at room temperature for 48 hr. Addition of the oxidation mixture to ice resulted in the formation of 0.5 g. of solid product. Evaporation of the solution gave an oil which could not be crystallized. Recrystallization of the solid product from ethanol gave *trans*-1,2-bis(*t*-butylsulfonyl) ethene, m.p. 228°.

Preparation of *cis*-1-Chloro-2-(*t*-butylmercapto)ethene.—Chloroacetylene was generated by dehydrohalogenation of *cis*-dichloroethylene with alcoholic potassium hydroxide according to the method of Ott.[8] *cis*-Dichloroethylene (15 g., 0.15 mole) in 75 ml. of absolute ethanol was added dropwise to a solution of potassium hydroxide (15 g., 0.25 mole) in 100 ml. of absolute ethanol while the generation flask was heated on a steam cone. The chloroacetylene which evolved was carried by a high purity nitrogen stream into the reaction flask which contained 150 ml. of absolute ethanol. A solution of 9.0 g. (0.10 mole) of *t*-butylmercaptan and 0.12 g. (0.050 g.-atom) of sodium in 50 ml. of absolute ethanol was added dropwise into the reaction flask during the generation of the chloroacetylene. Including the time of chloroacetylene addition, the reaction flask was heated for 3 hr. To prevent the escape of any unchanged chloroacetylene into the atmosphere, a trapping tower of an aqueous solution of 10 g. of mercuric cyanide and 4.6 g. of potassium hydroxide was attached to the system. After the reaction was complete, the system was opened with caution. The ethanol solution of the product was concentrated by evaporation of the ethanol and water added. The product was extracted with diethyl ether and the ether extracts dried with magnesium sulfate. The ether was then evaporated and the residue distilled under reduced pressure to yield 3.0 g. (0.020 mole) of *cis*-1-chloro-2-(*t*-butylmercapto)ethene, b.p. 87° (40 mm.), $n^{16}\mathrm{D}$ 1.5010.

The corresponding sulfone was prepared by treating 1.5 g. (0.020 mole) of the sulfide with 200 ml., 6.90 g. (0.050 mole) of a chloroform solution of perbenzoic acid. Recrystallization from water gave a solid melting at 77°.

Anal. Calcd. for $C_6H_{11}SO_2Cl$: C, 39.56; H, 6.05. Found: C, 39.60; H, 6.10.

The sulfone could also be prepared by oxidation with a hydrogen peroxide–acetic acid mixture, but it was necessary to evaporate the oxidation mixture to dryness before the sulfone could be obtained.

The infrared spectrum of *cis*-1-chloro-2-(*t*-butylmercapto)-ethene showed absorption at the following wave lengths: 3.35 (m), 3.50 (s), 6.05 (w), 6.43 (s), 6.60 (m), 6.90 (s), 7.20 (m), 7.35 (s), 7.80 (s), 8.23 (s), 8.65 (s), 9.30 (w), 9.85 (w), 12.15 (s, broad), 14–15.50 (s, broad) μ.

The infrared spectrum of *cis*-1-chloro-2-(*t*-butylsulfonyl)ethene showed absorption at the following wave lengths: 3.37 (m), 3.55 (m), 6.35 (s), 6.60 (m), 7.17 (w), 7.35 (w), 7.75 (s), 8.37 (m), 9.00 (s), 11.85 (s), 12.50 (w), 13.10 (s), 14.50 (s), 15.25 (m) μ.

Preparation of *t*-Butylmercaptoacetylene.—1-Chloro-2-(*t*-butylmercapto)ethene (2.5 g., 0.016 mole) was heated with solid potassium hydroxide to 70°. The product was then distilled at 2-mm. pressure and collected in a container immersed in a Dry Ice–acetone bath. Redistillation under reduced pressure gave 2.0 g. (0.015 mole) of *t*-butylmercaptoacetylene, b.p. 35° (40 mm.), $n^{16}\mathrm{D}$ 1.4678, lit.[9] b.p. 51.2–52.5° (72 mm.), $n^{25}\mathrm{D}$ 1.4667.

The infrared spectrum of *t*-butylmercaptoacetylene showed absorption at the following wave lengths: 3.10 (s), 3.45 (s), 4.95 (s), 6.90 (s), 7.35 (s), 8.22 (w), 8.60 (s), 12.45 (w), 14.85 (m, broad) μ.

Reaction of Sodium *t*-Butylmercaptide with *t*-Butylmercaptoacetylene.—*t*-Butylmercaptoacetylene (1.5 g., 0.013 mole) was mixed with a solution of 1.2 g. (0.013 mole) of *t*-butylmercaptan and 0.50 g. (0.013 g.-atom) of sodium in 50 ml. of absolute ethanol. The solution was refluxed for 1 hr. and then concentrated by evaporation of the ethanol. After diluting with water, the solid which formed was extracted with ether. The ether extracts were combined, dried with magnesium sulfate and the ether evaporated. By dissolution in acetic acid and precipitation with water 1.2 g. (0.0070 mole) of *cis*-1,2-bis(*t*-butylmercapto)ethene was obtained. The product was purified by crystallization from petroleum ether solution in a Dry Ice–trichloroethylene bath. A mixture melting point determination with a sample of *cis*-1,2-bis(*t*-butylmercapto)-ethene from the reaction of *cis*-dichloroethylene and sodium *t*-butylmercaptide showed no depression, m.p. 56–58°.

N.m.r. Apparatus and Procedure.—The equipment consisted of Varian A-60 spectrometer operating at a frequency of 60 Mc.p.s. Samples were run in deuteriochloroform at approximately 10% concentration. Tetramethylsilane was used as an internal standard and all values are referred to the proton signal of this compound.

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