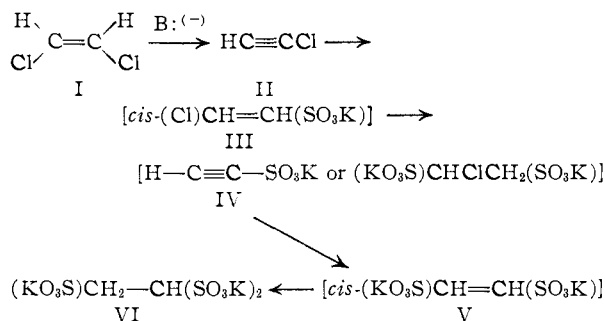




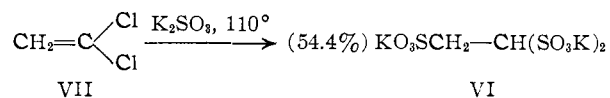
The following elimination-addition mechanism is thus favored<sup>16</sup>



*trans* addition of potassium sulfite to chloroacetylene (IIb) to give III is postulated on the basis that sodium *p*-toluenethiolate adds *trans* to IIb,<sup>2</sup> phenylacetylene<sup>17</sup> and *p*-tolylmercaptoacetylene.<sup>2</sup> Intermediates III, IV<sup>18</sup> and V were not isolated in this reaction, not even when using a large excess of chloroacetylene (IIb) or *cis*-dichloroethylene (I); the only product obtained was VI.

Since sulfite free radical, SO<sub>3</sub><sup>-</sup>, is known to add readily to olefinic systems,<sup>19</sup> it was necessary to rule out the possibility of a free-radical mechanism. Accordingly, diphenylamine, a free radical inhibitor, was added (1.83 wt. %), but it did not change the composition of the product or yield of the trisulfonate.<sup>20</sup>

**Vinylidene Chloride.**—Having investigated the 1,2-dichloroethylenes, it became of interest to study the behavior of the isomeric vinylidene chloride toward potassium sulfite. In a comparatively sluggish reaction,<sup>21</sup> vinylidene chloride (VII) reacted with potassium sulfite to give VI. This reaction was complicated by polymerization of vinylidene chloride.



An elimination-addition mechanism proceeding through chloroacetylene (IIb) was ruled out since

(16) Other mechanisms include the type usually postulated for ordinary aliphatic SN<sub>2</sub> reactions (C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 306-419). Drawbacks for such a mechanism in this case include the fact that direct displacements on vinyl halides are difficult,<sup>3</sup> and it does not explain the inertness of the *trans* isomer in the reaction under study. An explanation that could be offered is that the non-reactivity of *trans*-dichloroethylene is due to the greater shielding of the carbon atom which is being attacked.

An addition-elimination mechanism has been ruled out since it does not explain the inertness of *trans*-dichloroethylene in this reaction. One would predict that the same intermediate, (KO<sub>3</sub>S)CH(Cl)-CH<sub>2</sub>(Cl), would be obtained with comparable facility from both *cis*- and *trans*-dichloroethylene.

(17) W. E. Truce and J. A. Simms, *THIS JOURNAL*, **78**, 2756 (1956).

(18) The sulfonyl chloride, CH<sub>3</sub>CSO<sub>2</sub>Cl, has been referred to by C. S. Rondstedt, Jr., *THIS JOURNAL*, **76**, 1926 (1954).

(19) M. S. Kharasch, E. M. May and F. R. Mayo, *J. Org. Chem.*, **3**, 175 (1939).

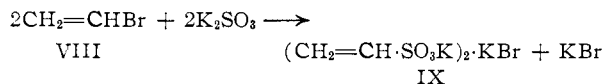
(20) The presence of ethylene glycol in the solvent system may inhibit the autoxidation of sulfite ion: L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 371; W. A. Waters, "The Chemistry of Free Radicals," Second Edition, The Clarendon Press, Oxford, 1948, p. 234.

(21) Vinylidene chloride did not react with potassium sulfite at 75°, while at 60°, *cis*-dichloroethylene reacted readily in almost quantitative conversion to VI.

FitzGibbon<sup>22</sup> reported that VII did not form IIa or any other mercury derivative when treated with alkaline mercuric cyanide (I forms mercuric chloroacetylide (IIa) under the same conditions) and upon repeating this work under a variety of conditions IIa could not be prepared from VII.

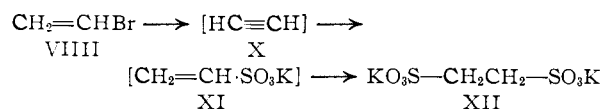
Possibly, an addition-elimination mechanism proceeding through the adduct (KO<sub>3</sub>S)CH<sub>2</sub>-CH(Cl)<sub>2</sub> is occurring. In an analogous reaction,<sup>23</sup> VII was shown to react with sodium *p*-toluenethiolate to give an intermediate, *trans*-(ArS)CH=CH(Cl). The latter presumably arises by a stereospecific *trans* elimination<sup>24</sup> from the isolated adduct, (ArS)CH<sub>2</sub>-CH(Cl)<sub>2</sub>.

**Vinyl Bromide.**—It has been claimed that the double salt IX is formed in the reaction<sup>7,25</sup>



However, we obtained only potassium 1,2-ethanedisulfonate in quantitative yield upon reaction of equimolecular amounts of these reactants. This structure is supported by its equivalent weight, determined by an ion-exchange method,<sup>3</sup> and by elemental analysis. Furthermore, its S-benzylthiuronium derivative did not depress the melting point of the same derivative prepared from an authentic sample of sodium 1,2-ethanedisulfonate.

Support for an elimination-addition mechanism for this reaction is offered by the patent claim<sup>26</sup> that acetylene (X) reacts with sulfites or bisulfites to give a mixture of XI and XII. The detection of X in those sealed tube reactions in which a twofold excess of vinyl bromide was used, lends additional support for this mechanism.<sup>27</sup> It also has been reported that intermediate XI can react with bisulfite to give XII.<sup>7</sup> The following sequence is suggested by these observations<sup>28</sup>



### Experimental<sup>29</sup>

In the work reported, C.P. potassium sulfite (J. T. Baker,

(22) M. FitzGibbon, *J. Chem. Soc.*, 1218 (1938).

(23) W. E. Truce and M. M. Boudakian, *THIS JOURNAL*, **78**, 2748 (1956).

(24) D. Y. Curtin, *Record of Chemical Progress*, **15**, 11 (1954); Abstracts, Thirteenth National Organic Chemistry Symposium, June, 1953, Ann Arbor, Michigan.

(25) C. M. Suter, "The Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 170.

(26) I. G. Farbenind, A.-G., French Patent 858,185 (November 19, 1940); *Chem. Zentr.*, **112**, I, 1738 (1941).

(27) Acetylene was found to be the only product of the reactions between vinyl bromide and the following nucleophilic agents: sodium ethoxide (61.3% conversion to acetylene); sodium methoxide (42.3%); aniline (42.0%); J. Loevenich, J. Losen and A. Dierichs, *Ber.*, **60**, 950 (1927).

(28) The possibility that the initial step may involve the addition of potassium sulfite to VIII to give potassium 2-bromoethanesulfonate has not been ruled out. Under free radical conditions (in the presence of oxygen and peroxides), 2-chloroethanesulfonate (89.6%) was obtained from vinyl chloride (1 mole) and sodium bisulfite (2 moles): J. E. Wicklatz, U. S. Patent 2,600,287 (June 10, 1952) (to Phillips Petroleum Co.).

(29) All boiling and melting points are uncorrected.

97.3% assay, the remainder being mainly potassium sulfate<sup>(30)</sup> was used. A correction was applied in all of our calculations, including iodometric titrations, for the purity of the sulfite.

*cis*-Dichloroethylene (Matheson) was fractionated through a Todd Column packed with glass helices (length, 90 cm.; inner diameter, 12 mm.), and a middle cut, b.p. 59.0° (737.0 mm.),  $n_D^{20}$  1.4481, was used. *trans*-Dichloroethylene (Matheson) was fractionally distilled in a similar manner, b.p. 48.3–48.6° (742.5 mm.),  $n_D^{20}$  1.4450. Comparison of the respective infrared spectra indicated no cross-contamination.<sup>31</sup>

In most of the experiments reported, the extent of reaction was followed by iodometric titration for sulfite ion.<sup>32</sup> This analytical method was standardized by using known mixtures of organic sulfonate, potassium sulfite, ethylene glycol and water. Our results indicate that sulfite ion could be determined iodometrically to within 1.5 to 4.0% of the known sulfite concentration.

As a supplementary analytical tool, ion exchange methods<sup>8</sup> were used in determining the equivalent weight of the organic sulfonate under study. A Dowex-50 (Nalcite HCR) ion exchange column was used (20–50 mesh, exchange capacity was found to be 1.26 meq./ml.). After titrating the effluent with standard base, the equivalent weight can be easily calculated. The method was standardized against known samples of sodium ethanesulfonate, sodium 1,2-ethanedisulfonate and potassium 1,1,2-ethanetrifluorosulfonate.

In all the sealed tube reactions, the tube was flushed with nitrogen before and after addition of the reactants.

**Reaction of *cis*-Dichloroethylene and Potassium Sulfite.**—A mixture of *cis*-dichloroethylene (0.05 mole, 4.85 g., 3.85 ml.), 14.25 g. (0.09 mole) of potassium sulfite, 10.0 ml. of ethylene glycol and 25.0 ml. of water was heated in a sealed Carius tube for 10.5 hours at 102°. After permitting the frozen contents of the opened tube to warm to room temperature, a slight detonation occurred and was accompanied by the deposition of carbonaceous material on the walls of the tube. Presumably this can be attributed to dehydrohalogenation of excess haloolefin to chloroacetylene, the latter being known to ignite and detonate upon contact with air.<sup>15</sup> Consequently, in later work, stoichiometric ratios were employed, thus avoiding further difficulty with the generation of chloroacetylene.

The reaction mixture was fractionally crystallized to give 10.16 g. (88.4% conversion) of an organic sulfonate.

*Anal.*<sup>33</sup> Calcd. for  $C_3H_3S_3O_9K_3$ : C, 6.25; O, 0.78; K, 29.70; equiv. wt., 128.18. Found: C, 6.65; H, 0.88; K, 29.70; equiv. wt. (ion exchange<sup>14</sup>), 134.3.

The S-benzylthiuronium derivative was prepared from 1.0 g. of the organic sulfonate and 2.0 g. of S-benzylthiuronium chloride. The crude product (2.01 g.) was recrystallized from water to give a material melting at 164.5–165.5°, undepressed by admixture with an authentic sample<sup>10</sup> of S-benzylthiuronium 1,1,2-ethanetrifluorosulfonate (m.p. 165.5–166.5°).

*Anal.* Calcd. for  $C_{26}H_{36}O_9N_6S_6$ : C, 40.61; H, 4.72; N, 10.93. Found (lower melting form): C, 40.60; H, 4.72; N, 10.75.

After standing for 4 months, the S-benzylthiuronium derivative obtained from *cis*-dichloroethylene and potassium sulfite had reverted to a higher melting form, m.p. 195.5–196.5°.

*Anal.* Calcd. for  $C_{26}H_{36}O_9N_6S_6$ : C, 40.61; H, 4.72; N, 10.93. Found (higher melting form): C, 40.87; H, 4.91; N, 11.11.

(30) Private communication, Laboratory Chemical Division, J. T. Baker Chemical Co. In some of our earlier work, potassium sulfite was prepared by the neutralization of potassium pyrosulfite,  $K_2S_2O_8$ , with potassium hydroxide; "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, pp. 166–167.

(31) H. M. Randall, N. Fuson, R. G. Fowler and J. R. Dangle, "Infrared Determination of Organic Substances," D. Van Nostrand Co., Inc., New York, N. Y., 1949, pp. 46–65.

(32) A. I. Vogel, "A Textbook of Quantitative Inorganic Analysis," Longmans, Green and Co., London, Second Edition, 1951, p. 354; W. C. Pierce and E. L. Haenisch, "Quantitative Analysis," Third Edition, John Wiley and Sons, Inc., New York, N. Y., 1948, pp. 237, 242.

(33) Analyses were done by Dr. C. S. Yeh and Mrs. Jean Fortney of the Purdue University Chemistry Microanalytical Laboratory.

This phenomenon can also be observed by repeatedly recrystallizing the lower melting form from water.

***cis*-Dichloroethylene and Potassium Sulfite in the Presence of Diphenylamine.**—To preclude the possibility of a free radical mechanism, the reaction between *cis*-dichloroethylene (2.91 g., 2.29 ml., 0.03 mole) and potassium sulfite (14.25 g., 0.09 mole) in 10.0 ml. of ethylene glycol and 25.0 ml. of distilled water was repeated in the presence of 1.0 g. of diphenylamine (1.83 wt. %) and run for 119.5 hours at 100°. The contents of the tube were diluted with 250 ml. of distilled water, the diphenylamine was extracted with petroleum ether (30–60°) and the reaction mixture was poured into a 500-ml. volumetric flask and diluted to the 500-ml. mark with distilled water. Titration against 10.00 ml. of iodine solution (0.10377 *N*) for two separate determinations required 34.60 ml. and 34.90 ml., which represented, respectively, 1.19 g. (8.10%) and 1.18 g. (8.03%) of potassium sulfite. The reaction mixture was concentrated and fractionally crystallized to give 8.82 g. of an organic sulfonate (conversion to the trisulfonate, 88.8%; yield 96.6%), whose S-benzylthiuronium derivative melted at 196.0–196.5°.

**Reaction of 1,1,2-Trichloroethane and Potassium Sulfite.**—An independent synthesis of potassium 1,1,2-ethanetrifluorosulfonate<sup>10</sup> was carried out by treating 40.1 g. (0.30 mole) of 1,1,2-trichloroethane (Eastman Kodak Co., b.p. 111.8–111.9° (735 mm.),  $n_D^{20}$  1.4705) and 142.5 g. (0.90 mole) of potassium sulfite in 300 ml. of ethylene glycol and 250 ml. of water at 70–75° for 24 hours. The reaction mixture was cooled to room temperature and an organic sulfonate (wt. 25.98 g., 22.5% conversion<sup>34</sup>) was filtered off. Crop I was further crystallized from water, using Norite A.

*Anal.* Calcd. for  $C_3H_3S_3O_9K_3$ : C, 6.25; H, 0.78; K, 29.70. Found: C, 6.30; H, 1.04; K, 29.45.

Ion exchange analysis<sup>8</sup> was used to determine the equivalent weight: calcd. 128.18; found 134.9.

The S-benzylthiuronium derivative was prepared from 1.0 g. of the organic sulfonate and 2.0 g. of S-benzylthiuronium chloride to give 1.33 g. of product, which was recrystallized from water, using Norite A; m.p. 164.0–165.5°.

*Anal.* Calcd. for  $C_{26}H_{36}O_9N_6S_6$ : C, 40.61; H, 4.72; N, 10.93. Found: C, 40.01; H, 4.74; N, 11.21.

No depression was observed upon admixture with the S-benzylthiuronium 1,1,2-ethanetrifluorosulfonate (lower melting form) from *cis*-dichloroethylene and potassium sulfite. Upon standing for 4 months, this derivative (from 1,1,2-trichloroethane and potassium sulfite) reverted to a higher-melting modification, m.p. 194.5–196.0°. This can also be effected by repeated recrystallization from water.

**Preparation of 1,1,2-Ethanetrifluorosulfonic Acid.**—Potassium 1,1,2-ethanetrifluorosulfonate (1.013 g., 0.0026 mole), prepared from 1,1,2-trichloroethane and potassium sulfite, was dissolved in 25.0 ml. of distilled water and passed through an ion exchange column (Dowex-50–Nalcite HCR), and the effluent was evaporated to a viscous yellow liquid, which was further dried over phosphorus pentoxide under vacuum. No crystallization of this liquid (wt. 0.71 g.; theoretical, 0.745 g.) occurred, but crystallization did set in upon cooling in a refrigerator, m.p. 100–110° (sealed capillary) with apparent decomposition. A crude sample of this acid has been reported to melt at 80–110°.<sup>10</sup>

***trans*-Dichloroethylene and Potassium Sulfite.**—The following reactants were charged into a Carius tube: potassium sulfite (0.09 mole, 14.25 g.), *trans*-dichloroethylene (0.03 mole, 2.91 g., 2.31 ml.), 10.0 ml. of ethylene glycol and 25.0 ml. of distilled water, and heated for 93.5 hours at 60.4° (refluxing chloroform at 746 mm.). The contents of the tube were poured into a separatory funnel, diluted with water, and the haloolefin layer removed (1.57 g., 54.0% recovery,  $n_D^{20}$  1.4450). The reaction mixture was diluted to the 250-ml. mark with water, and then titrated against 50.00 ml. of standardized iodine (0.10377 *N*). For two separate titrations, 7.48 and 7.50 ml. of solution were required, representing, respectively, 13.72 (96.30%) and 13.69 g. (96.05%) of potassium sulfite. The reaction mixture was concentrated and fractionally crystallized to give 0.70 g. (6.05% conversion) of potassium 1,1,2-ethanetrifluorosulfonate, whose S-benzylthiuronium derivative melted at 195.5–196.5°.

*Anal.* Calcd. for  $C_{26}H_{36}O_9N_6S_6$ : C, 40.61; H, 4.72; N, 10.93. Found: C, 40.19; H, 4.66; N, 10.91.

(34) A 56.3% conversion to the trisulfonate was obtained when 1,1,2-trichloroethane was used.

Under identical conditions at 60° for 93.5 hours, the following data were obtained for *cis*-dichloroethylene: no unreacted haloolefin was recovered; iodometric analysis (0.10377 *N*) showed that only 6.23% of the original sulfite was left; 9.62 g. (83.5% conversion, 88.8% yield) of potassium 1,1,2-ethanetrifluorates whose S-benzylthiuronium derivative melted at 195.5–196.5°.

**Reaction of Chloroacetylene with Potassium Sulfite.**—Mercuric bis-(chloroacetylde) (IIa)<sup>29,15,22</sup> (10.1 g., 0.0317 mole) was decomposed by slowly adding a solution of potassium hydroxide (4.0 g., 0.0713 mole) and potassium cyanide (20.0 g., 0.23 mole), while the generation flask was heated on a steam-cone, and the evolved chloroacetylene was carried in hydrogen or nitrogen (de-oxygenated by passage through Fieser solution<sup>35</sup>). The gas stream was passed into a reaction flask containing 14.85 g. (0.0939 mole) of potassium sulfite in 60 ml. of ethylene glycol, 150 ml. of distilled water and 100 ml. of 95% ethanol.<sup>36</sup> To prevent escape of any unreacted chloroacetylene into the atmosphere, a trapping tower consisting of 10.0 g. (0.0397 mole) of mercuric cyanide and 4.6 g. (0.082 mole) of potassium hydroxide in 50 ml. of water was used. The reaction mixture was heated to reflux for 9 hours. After 25 minutes, a white precipitate appeared in the trapping tower and, after one hour, a yellow flame characteristic of chloroacetylene was ejected from the outlet attached to the drying tower. This was corrected by attaching additional trapping towers. The "inert" gas stream was maintained overnight to entrain any residual chloroacetylene. The contents of the trapping towers were filtered to give 3.40 g. (33.7%) of recovered mercuric chloroacetylde. The alcohol was evaporated and the concentrated reaction mixture was diluted to exactly one liter with distilled water. Titration against 25.00 ml. of standardized (0.10 351 *N*) iodine solution required 26.65 and 26.73 ml. of the diluted reaction mixture. This represents, respectively, 7.68 (51.74%) and 7.66 g. (51.59%) of recovered potassium sulfite.

The remainder of the reaction mixture was concentrated and fractionally crystallized. Nine different crops were obtained, each of which gave an S-benzylthiuronium derivative melting in the range 194.0–196.5°. There was no depression with an authentic sample of S-benzylthiuronium 1,1,2-ethanetrifluorates (m.p. 195.0–196.0° form used). The combined weight of crops I through IX was 6.84 g. (56.7% conversion to the trifluorates).

**Reaction of Vinylidene Chloride<sup>37</sup> and Potassium Sulfite.**—Having distilled 2.91 g. (0.03 mole) of vinylidene chloride (b.p. 31.0° (748 mm.)) through a short glass-helix-packed column into a Carius tube, 9.49 g. (0.06 mole) of potassium sulfite in 10.0 ml. of ethylene glycol and 25.0 ml. of distilled

(35) L. F. Fieser, "Experiments in Organic Chemistry," Second Edition, D. C. Heath and Co., New York, N. Y., 1941, pp. 395–396.

(36) The addition of 95% ethanol markedly enhances the solubility of chloroethylene in the reaction mixture. In a similar experiment, but in the absence of ethanol, only a 4.82% conversion to potassium 1,1,2-ethanetrifluorates was effected.

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

water and 0.25 g. of diphenylamine (0.50 wt. %), a polymerization inhibitor, were added. The sealed tube was heated at 110° for 45.0 hours. Polyvinylidene chloride (0.33 g., 11.2%) was filtered from the reaction mixture and diphenylamine was removed by extraction with petroleum ether (b.p. 30–60°). After diluting the reaction mixture to one liter, titration against 25.00 ml. of iodine solution (0.10377 *N*) required 75.30 and 75.20 ml., representing, respectively, 2.726 (28.71%) and 2.730 g. (28.75%) of recovered potassium sulfite. The reaction mixture was concentrated and fractionally crystallized to give 4.18 g. (54.3% conversion to the trifluorates) of an organic sulfonate whose S-benzylthiuronium derivative melted at 195.0°, undepressed by an authentic sample of S-benzylthiuronium 1,1,2-ethanetrifluorates. In an earlier run, the lower melting S-benzylthiuronium derivative of VI, m.p. 164.5–165.5°, was obtained, but on standing reverted to the higher melting form.

**Reaction of Vinyl Bromide and Potassium Sulfite.**—Vinyl bromide (Matheson, 5.34 g., 3.53 ml., 0.05 mole) was distilled into a Carius tube. Potassium sulfite (7.92 g., 0.05 mole) in 10.0 ml. of ethylene glycol and 25.0 ml. of distilled water was added. The sealed tube was heated at 135° for 38.0 hours. Applying the heated end of a glass rod to the scratched tip of the frozen Carius tube caused a mild detonation, and a subsequent appearance of a yellow flame which lasted for about 15 seconds. This was presumably caused by the formation of acetylene in the reaction mixture. The reaction mixture was filtered (wt. of polyvinyl bromide, 0.10 g., 1.87%), and the filtrate was diluted with water to exactly 500 ml. A 10.00-ml. aliquot was equivalent to 0.01 ml. of iodine solution (0.10351 *N*), indicating that only 0.004 g. (0.052%) of potassium sulfite was left. The reaction mixture was concentrated and fractionally crystallized.

Seven different crops of an organic sulfonate were obtained (6.63 g., 99.6% conversion).

*Anal.* Calcd. for C<sub>2</sub>H<sub>4</sub>O<sub>6</sub>S<sub>2</sub>K<sub>2</sub>: C, 9.02; H, 1.51; K, 29.35; equiv. wt., 133.19. Found: C, 9.35; H, 1.63; K, 29.68; equiv. wt. (ion exchange), 137.5.

The S-benzylthiuronium derivative for each of the 7 crops melted in the range 199–202° (reported<sup>38</sup> 201–202°).

*Anal.* Calcd. for C<sub>18</sub>H<sub>24</sub>S<sub>4</sub>N<sub>4</sub>O<sub>6</sub>: C, 41.36; H, 5.01; N, 10.72. Found (m.p. 201–202°): C, 41.42; H, 4.90; N, 10.94.

No depression was observed with the same derivative from sodium 1,2-ethanedithiolate (m.p. 201–202°).

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(38) W. F. Whitmore and E. F. Landau, *THIS JOURNAL*, **68**, 1797 (1946). The S-benzylthiuronium derivative of ethylenesulfonic acid melts at 145–146°.