

of potassium hydroxide was used except for the variations stated in Tables I, II and III. These materials were added to 40 ml. of U.S.P. ethanol and refluxed on a water-bath for 2 hr. in a 150-ml. r.b. flask fitted with a reflux condenser. The hot reaction mixtures were then poured in ice-water and the 3a,6a-diphenylglycolurils precipitated. These precipitates were filtered onto tared filter papers and dried over calcium chloride in a desiccator for 2 days before weighing. The samples were then recrystallized from glacial acetic acid. The first product obtained was analyzed by nitrogen determination and subsequent products were characterized by their melting points. All samples melted in the range 390–394°. According to the literature<sup>3</sup> 3a,6a-diphenylglycoluril fails to melt at 330°.

*Anal.* Calcd. for C<sub>16</sub>H<sub>14</sub>O<sub>2</sub>N<sub>4</sub>: N, 19.09. Found: N, 18.70.

The filtrates from the glycoluril filtrations were then acidified with concentrated hydrochloric acid and the 5,5-diphenylhydantoin was precipitated. These were isolated and dried as above. The samples were recrystallized from ethanol. The identities of the products were checked in the same manner as were the glycolurils. All samples melted in the range 289–293°. The literature m.p. of 5,5-diphenylhydantoin is given as 293°.<sup>17</sup>

**Attempted Condensation of Benzil with Urea in Neutral Solution.**—An identical reaction to those previous was run except that no alkali was added. Addition of water to the reaction mixture produced a light yellow precipitate of fine needle-like crystals weighing 1.94 g. and melting at 93–95°, which was identical with the starting benzil.

**Attempted Condensation of Benzil with Urea in Acidic Solution.**—Another identical reaction was run except that 1 ml. of concentrated hydrochloric acid was substituted for the potassium hydroxide. Addition of water brought down a light yellow precipitate weighing 1.98 g. which melted at 94–96°, again unreacted benzil.

**Condensation of 4,4'-Disubstituted Benzils with Urea.**—All of the benzils listed in Table IV were refluxed with urea and ethanolic potassium hydroxide. Reaction mixtures consisted of 0.095 mole of the benzil, 0.016 mole of urea

and 0.017 mole of potassium hydroxide in 40 ml. of U.S.P. ethanol. They were refluxed for 2 hr. and then worked up in the same manner as the reaction products of benzil and urea. The new products resulting are characterized in Table V.

TABLE V

Compound	M.p., °C.	Nitrogen, % Calcd.	Nitrogen, % Found
3a,6a-Di-(4-ethoxyphenyl)-glycoluril	147–149	14.65	14.26
5,5-Di-(4-ethoxyphenyl)-hydantoin	195–198	8.23	8.21
3a,6a-Di-(4-bis-dimethylaminophenyl)-glycoluril	199–201	22.09	22.01
3a,6a-Di-(4-acetamidophenyl)-glycoluril	237–239	20.51	20.50
3a,6a-Di-(4-phenoxyphenyl)-glycoluril	215–217	11.71	10.08
5,5-Di-(4-phenoxyphenyl)-hydantoin	182–185	6.43	6.27
5,5-Di-(4-chlorophenyl)-hydantoin	226–230	8.83	8.81
3a,6a-Di-(4-chlorophenyl)-glycoluril	285–287	15.43	15.43

**Rearrangement of III to II in Acidic Solution.**—4,5-Diphenyl-4,5-dihydroxy-2-imidazolone (III) was prepared by the method of Breur and Zincke.<sup>18</sup> The material melted at 169–170°. The literature decomposition point<sup>18</sup> is 170°.

One gram of III was added to 30 ml. of U.S.P. ethanol containing 1 ml. of concentrated sulfuric acid. The mixture was thoroughly mixed and refluxed for 2 hr. on a water-bath. Upon pouring into cold water a precipitate of II formed weighing 0.32 g. (34%) which, after recrystallization from ethanol, decomposed at 169–170°.

**Attempted Rearrangement of III in Neutral Solution.**—The same procedure as above was carried out using 0.5 g. of III and omitting the acid. Upon pouring the reaction mixture into cold water, a white flocculent precipitate formed weighing 0.48 g. and melting at 200° (III).

**Acknowledgment.**—We are indebted to A. L. Ippolito for the preparation of the 4,4'-disubstituted benzils and to Miami University for financial assistance in conducting this study.

OXFORD, OHIO

(18) A. Breur and T. Zincke, *ibid.*, **198**, 151 (1879).

(17) H. Biltz, *Ann.*, **368**, 243 (1909).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

## Stereospecific Reactions of Nucleophilic Agents with Acetylenes and Vinyl-type Halides. I. The Mechanism of the Base-catalyzed Reaction of *cis*-Dichloroethylene with Thiols<sup>1</sup>

BY WILLIAM E. TRUCE, MAX M. BOUDAKIAN, RICHARD F. HEINE AND ROBERT J. McMANIMIE

RECEIVED OCTOBER 21, 1955

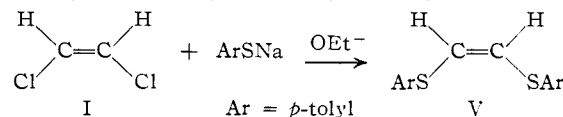
Evidence, both kinetic and chemical, is presented to account for the stereospecific conversion of *cis*-dichloroethylene (I) to *cis*-1,2-bis-(*p*-tolylmercapto)-ethene (V). The proposed reaction sequence is presented in the Introduction as an elimination-addition mechanism. The conversion of chloroacetylene (II) to III, and *p*-tolylmercaptoacetylene (IV) to V, constitute stereospecific *trans* nucleophilic additions across a triple bond.

### Introduction

There are several reports that *cis*-dichloroethylene (I) reacts readily with nucleophilic agents such as sodium benzenethiolate,<sup>2,3</sup> sodium *p*-toluenethiolate,<sup>2</sup> sodium 2-methyl-2-propanethiolate<sup>4</sup> and potassium sulfite,<sup>5</sup> while the *trans* isomer, when treated likewise, is recovered unchanged.

The detailed mechanisms of the reactions of nucleophilic agents with the dichloroethylenes were

unknown and constitute the purpose of this and later papers. The reaction chosen for this study was the one obtained with the thiolates<sup>2</sup>



Three important observations bearing on the mechanism of this reaction are (a) *trans*-dichloroethylene does not react, (b) sodium ethoxide is necessary in order for any reaction to occur and (c) the final product has exclusively the *cis* structure. The following three mechanisms were considered for the conversion of *cis*-dichloroethylene (I) to *cis*-bis-(arylmercapto)-ethene (V).

**A. Nucleophilic Displacement Mechanism.**—One possible reaction path is an S<sub>N</sub><sup>2</sup> process

(1) This paper was presented in part before the Division of Organic Chemistry at the Fall 1955 Meeting of the American Chemical Society in Minneapolis, Minn. Abstracted in part from the Ph.D. Thesis of Max M. Boudakian and from the M.S. Thesis of Richard F. Heine.

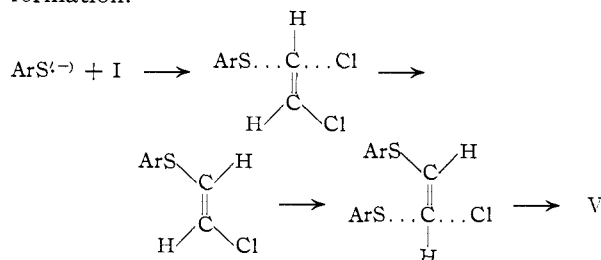
(2) W. E. Truce and R. J. McManimie, *THIS JOURNAL*, **76**, 5745 (1954).

(3) W. E. Parham and J. Heberling, *ibid.*, **77**, 1175 (1955).

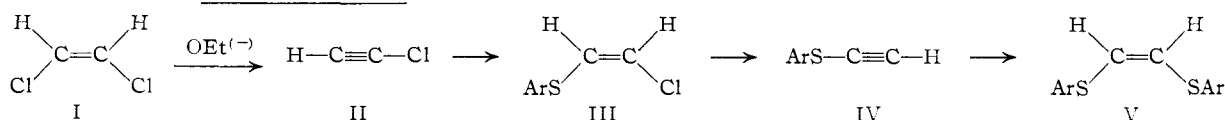
(4) H. J. Backer and J. Strating, *Rec. trav. chim.*, **73**, 565 (1954).

(5) W. E. Truce and M. M. Boudakian, *THIS JOURNAL*, **78**, 2752 (1956).

analogous to that encountered with saturated aliphatic compounds.<sup>6</sup> In view of the powerful nucleophilicity of arylthiolates,<sup>7</sup> a direct displacement of chloride ion could account for this transformation.

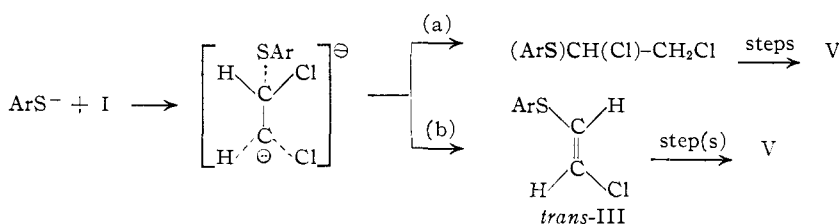


Such a mechanism suffers from the fact that direct displacements on vinyl halides are difficult.<sup>7c,8,9</sup>



Furthermore, it does not explain the inertness of the *trans* isomer<sup>10</sup> nor the lack of any reaction in the absence of sodium ethoxide.

**B. Addition-Elimination Mechanism.**—Another possible sequence is an addition-elimination mechanism as outlined



In regard to sequence (a), one would expect the highly nucleophilic arylthiolate ion<sup>7</sup> to give the same adduct,  $(\text{ArS})\text{CH}(\text{Cl})-\text{CH}_2\text{Cl}$ , with *trans*-dichloroethylene. Reaction path (b) to *trans*-III which is analogous to the mechanism postulated for aromatic nucleophilic substitution reactions,<sup>7c</sup> can be rejected on the basis that *trans*-III, which had been previously synthesized from acetylene and *p*-toluenesulfonyl chloride<sup>11,12</sup> when treated with sodium *p*-toluenethiolate in the presence of sodium ethoxide, gave only a 10.2% conversion to V. Since *cis*-dichloroethylene (I) reacts under the same

(6) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 306-419.

(7) (a) O. R. Quayle and E. E. Royals, *THIS JOURNAL*, **64**, 226 (1942); (b) P. B. D. de la Mare and C. A. Vernon, *J. Chem. Soc.*, 3331 (1952); (c) J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 297 (1951); (d) J. Hine and W. H. Brader, *THIS JOURNAL*, **75**, 3964 (1953); (e) J. F. Bunnett and G. T. Davis, *ibid.*, **76**, 3011 (1954).

(8) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 153.

(9) A. G. Catchpole, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 10 (1948).

(10) This could be due to greater shielding of the carbon atom which is attacked.

(11) Such adducts have been assigned a *trans* structure; N. Kharasch and S. J. Assony, *THIS JOURNAL*, **77**, 3390 (1955); **75**, 1081 (1953).

(12) For chemical, as well as infrared, evidence on this configurational assignment, see W. E. Truce and M. M. Boudakian, *ibid.*, **78**, 2748 (1956).

conditions to give V in quantitative yield,<sup>2</sup> *trans*-III could not be an intermediate.

**C. Elimination-Addition Mechanism.**—Arguments in favor of this mechanism are that it explains why only the more readily dehydrohalogenated *cis*-haloolefin<sup>13-15</sup> reacted and why a strong base, sodium ethoxide, was required for any reaction to occur.

Several reservations must be made regarding such a reaction sequence. Previous workers reported little tendency on the part of chloroacetylene to react in any manner whatsoever with nucleophilic agents.<sup>16</sup> Furthermore, the postulated stereospecific *trans* nucleophilic additions to intermediates II and IV would give the presumably less-stable *cis*-olefins III<sup>17</sup> and V,<sup>17</sup> respectively, by this mechanism.<sup>18</sup>

## Discussion of Results

The direct displacement and addition-elimination mechanisms can be rejected on the basis of rate data and the behavior of the intermediates postulated for the elimination-addition mechanism.

**Kinetic Evidence.**—The rate of the reaction under study was found to be proportional to the concentrations of both the haloolefin and the ethoxide but was independent of the arylthiolate concentration (except at very low concentrations).<sup>19</sup> A rate expression was derived from a consideration of the equations

(13) G. Chavanne, *Bull. soc. chim. Belges*, **26**, 287 (1912); **28**, 234 (1914).

(14) F. Martin and Z. Bruylants, *ibid.*, **60**, 259 (1951).

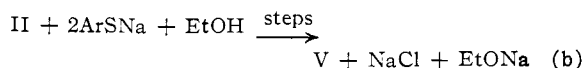
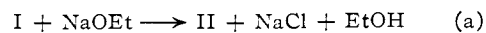
(15) S. I. Miller and R. M. Noyes, *THIS JOURNAL*, **74**, 629 (1952).

(16) (a) J. A. Nieuwland and R. R. Vogt, "The Chemistry of Acetylene," A.C.S. Monograph No. 99, Reinhold Publishing Corp., New York, N. Y., 1945, p. 71; "Replacement of the halogen in haloacetylenes by reaction with alkali sulfides, cyanides or thiocyanides, or with the alkali salts of alcohols, phenols, oxyacids or mercaptans have not been reported . . ." (b) E. Ott, G. Dittus and H. Weissenburger, *Ber.*, **76**, 87 (1943); ammonia and chloroacetylene do not react in the cold; with aniline (100 g.), 2.7 g. of indole are obtained, in addition to recovery of aniline (84.0 g.) and aniline hydrochloride (6.8 g.); with diethylamine, a product was obtained which was not isolated, but which was autoxidized to diethylformamide. (c) J. Loevenich, J. Losen and A. Dierichs, *ibid.*, **60**, 950 (1927); it was inferred that bromoacetylene did not react with aniline, nor with methoxide, ethoxide and ethanethiolate ions.

(17) The product *cis*-V has been thermally isomerized to the *trans* isomer by slow distillation<sup>2</sup>; vinylidene chloride and sodium *p*-toluenethiolate gave only *trans*-III, the latter presumably arising by a stereospecific *trans* elimination from  $(\text{C}_2\text{H}_3\text{S})\text{CH}_2\text{CH}(\text{Cl})_2$ , which was also obtained in the reaction.<sup>15</sup> (See D. Y. Curtin, *Record of Chemical Progress*, **16**, 111 (1954); Abstracts, 13th National Organic Chemistry Symposium, American Chemical Society, Ann Arbor, Mich., June, 1953.

(18) See G. W. Wheland, "Advanced Organic Chemistry," Second Edition, John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 303-306, for stereospecific *trans* additions by electrophilic agents across triple bonds.

(19) For low concentrations of the arylthiolate it may be possible that a step or steps embodied in equation (b) might be slower than (a), in which case ethoxide ion would not be regenerated as fast as it is consumed. In fact at vanishingly low arylthiolate concentrations the observed rate deviated from pseudo first order kinetics.



If (a) is assumed to be the slow step and the reactions embodied in (b) faster than (a), *i.e.*, rate  $b \gg$  rate a, then

$$(-) \frac{d(c + c_0)}{dt} \equiv (-) \frac{dc}{dt} = k_a c c_A$$

where  $c$  = concn. of I and  $c_A$  = concn. of ethoxide. If rate  $b \gg$  rate a, then sodium ethoxide will be regenerated nearly as fast as it is consumed and  $k_a c_A = k'$ , and the expression simplifies to

$$(-) \frac{dc}{dt} = k'c$$

This is the expression for a first-order reaction and when the experimental values of  $(-)\log c$  were plotted against time, a straight line was obtained. Table I includes the rate constant obtained for several different concentrations of sodium ethoxide.

TABLE I  
CONCENTRATION OF *cis*-DICHLOROETHYLENE (I), 0.133 MOLES/L.; TEMPERATURE,  $56.9 \pm 0.1^\circ$

Run	Concn. sodium ethoxide, mole l. <sup>-1</sup>	$k'$ , moles l. <sup>-1</sup> min. <sup>-1</sup> $\times 10^4$
1	0.042	7.6
2	.160	7.4
3	.201	7.6
4	.244	7.9

These data are more graphically described in Fig. 1. When the slopes of the lines obtained from the plots of  $(-)\log c$  vs.  $t$  are plotted against  $c_A$  (sodium ethoxide concentration), a straight line is obtained passing through the origin as shown in Fig. 2. The first-order dependence of the rate of reaction on sodium ethoxide concentration is clearly shown by this result.

These kinetic results lead to the conclusion that the first step in the reaction is a dehydrohalogenation, but do not offer any evidence regarding subsequent steps. From rate constants at three temperatures, the Arrhenius activation energy over the range  $56.9$  to  $72.0^\circ$  was found to be  $34.0 \pm 1.0$  kcal./mole. It is interesting to note that Miller and Noyes<sup>15</sup> report an activation energy for the dehydrohalogenation of *cis*-dichloroethylene using sodium methoxide in methanol of  $35.1 \pm 0.3$  kcal./mole (temperature range  $58.25$  to  $85.36^\circ$ ). The closeness of this figure to that obtained in the present study may be offered as secondary evidence for an initial dehydrohalogenation; in fact, the direction of the difference might be expected in view of the presumably greater basicity of ethoxide compared to methoxide ion.

**Chemical Evidence for Intermediates III and IV.**—To verify the intermediacy of chloroacetylene (II) in the reaction of I with sodium *p*-toluenethiolate to give V, chloroacetylene (II) was slowly generated and passed into an alcoholic solution prepared from various ratios of *p*-toluenethiol to sodium. The ratio of arylthiol to sodium controlled the extent to which the various intermediates could react further. In one experiment, II was treated with equimolecular amounts of arylthiol and sodium to give V (52.2% conversion, 77.4% yield), in addition to a liquid, which was

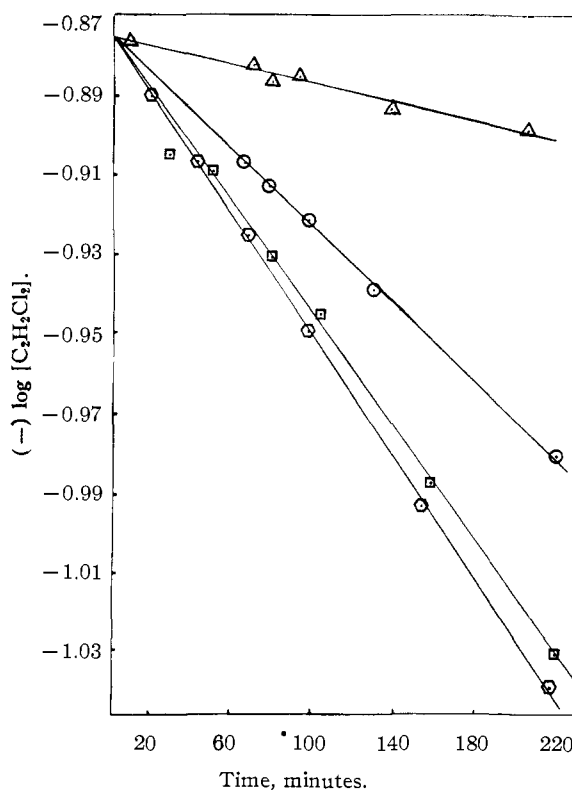


Fig. 1.—Plot showing dependency of rate of decrease of *cis*-dichloroethylene concentration as a function of concentration of sodium ethoxide:  $\Delta$ , run 1;  $\circ$ , run 2;  $\square$ , run 3;  $\diamond$ , run 4.

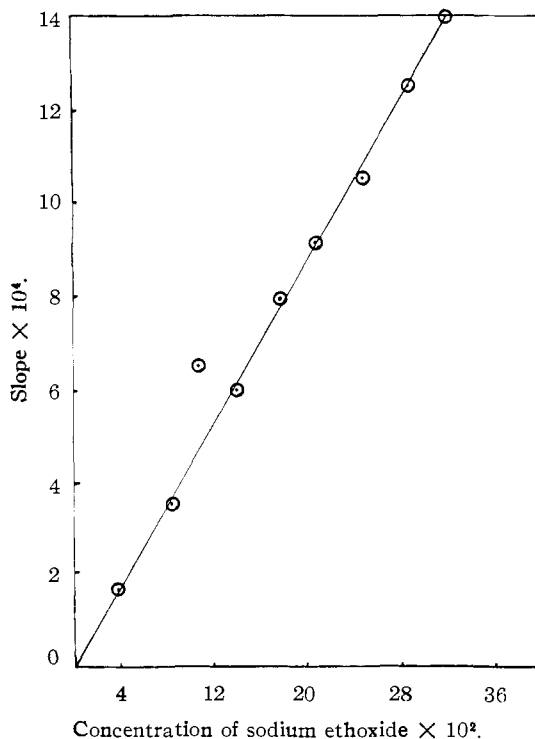


Fig. 2.—Slope of lines obtained from plots as in Fig. 1 plotted against sodium ethoxide concentration (concentration of sodium *p*-toluenethiolate: 0.150 mole/liter).

identified and characterized as *cis*-1-chloro-2-(*p*-tolylmercapto)-ethene (III) (13.7% conversion, 20.3% yield) as a result of the following arguments: (a) No  $>C=CH_2$  bands were present, thus ruling out a 1,1-disubstituted olefin.<sup>20,21</sup>

(b) The sulfone of this intermediate depressed the melting point of *trans*-1-chloro-2-(*p*-tolylsulfonyl)-ethene.<sup>12</sup>

(c) The assignment of the *cis* structure is also supported by the analogous *trans* addition of alcoholic sodium *p*-toluenethiolate to phenylacetylene to give *cis*-(C<sub>6</sub>H<sub>5</sub>)CH=CH(SC<sub>6</sub>H<sub>7</sub>),<sup>22</sup> and to *p*-tolylmercaptoacetylene (IV) to give V.

(d) It has been reported that *cis*-alkylhaloolefins have in-plane bending bands in the region 7.65–7.78  $\mu$ .<sup>23</sup> The compound under study had a strong infrared absorption band at 7.78  $\mu$ , which was absent in the spectrum of the *trans* isomer as prepared from acetylene and *p*-toluenesulfonyl chloride.<sup>12</sup>

(e) Finally, *cis*-III did not react with sodium *p*-toluenethiolate in the absence of sodium ethoxide, while in the presence of the latter, V was obtained in 98.3% yield (no *p*-toluenethiol recovered). This demonstrates the base-dependency of the conversion of III to V. *trans*-III<sup>12</sup> also did not react with sodium *p*-toluenethiolate in the absence of sodium ethoxide, but gave V in only 10.2% conversion (89.4% recovery of *p*-toluenethiol) when ethoxide was used.<sup>24</sup> By application of the rule of *trans* elimination<sup>25–27</sup> to this base-catalyzed reaction, the liquid intermediate III is assigned the *cis* structure. The base-dependency of the conversion of III to V was further demonstrated when treatment of chloroacetylene (II) with *p*-toluenethiol and half the amount of sodium previously used gave a considerably lower amount of V (49.2% yield), and a commensurate increase in III (47.4% yield).

Of particular significance was the indication (by the presence of infrared bands at 3.08 and 4.90  $\mu$ <sup>20,28</sup>) of a small amount of *p*-tolylmercaptoacetylene (IV) in the forerun of III. Like authentic IV, which also showed the same absorption bands, this forerun turned dark on standing, even at 0°. Furthermore, treatment with alkaline mercuric iodide reagent gave a mercury derivative (62.8% yield) which did not depress the melting point of mercuric bis-(*p*-tolylmercaptoacetylde), Hg—(C≡C—SC<sub>6</sub>H<sub>7</sub>)<sub>2</sub>.<sup>29</sup>

An authentic sample of intermediate IV was prepared and, on treatment with sodium *p*-toluenethio-

(20) F. A. Miller, in H. Gilman, "Organic Chemistry," Vol. III, Chapter 2, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 144.

(21) R. E. Kitson, *Anal. Chem.*, **25**, 1470 (1953).

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

(23) K. E. Harwell and L. F. Hatch, *ibid.*, **77**, 1682 (1955).

(24) When *trans*-III is treated with alkaline mercuric iodide reagent no mercuric bis-(*p*-tolylmercaptoacetylde) is formed, not even under sealed tube conditions. In contrast, *cis*-III does form this mercury derivative (52.3% yield).

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

(26) P. Pfeiffer, *Z. physik. Chem.*, **48**, 40 (1904).

(27) P. F. Frankland, *J. Chem. Soc.*, 654 (1912).

(28) J. H. Wotiz and F. A. Miller, *THIS JOURNAL*, **71**, 3441 (1949).

(29) Isolation only of this mercury derivative would not constitute evidence for the presence of traces of *p*-tolylmercaptoacetylene (IV) in the forerun, since treatment of pure *cis*-III with alkaline mercuric iodide gave mercuric bis-(*p*-tolylmercaptoacetylde) in 52.3% yield. See also S. J. Cristol, A. Begoon, W. P. Norris and P. S. Ramey, *ibid.*, **76**, 4558 (1954), for a similar case.

late, gave exclusively V (77.2% conversion). The same result (74.9% conversion) was obtained in the presence of a free radical inhibitor, diphenylamine (0.06 wt. %).

### Experimental<sup>30</sup>

**Procedure for Kinetic Runs.**—One of the methods considered for determining the kinetics of the reaction involved the measurement of chloride formation. However, thiulates interfere in most chloride determinations and good separation is difficult. Therefore, it was decided to measure the rate of decrease in base concentration. In order to use this method it was assumed that the concentration of sodium ethoxide remained constant (*i.e.*, rate of equation a  $\ll$  rate of equation b) and that the decrease in base concentration is equivalent to the decrease in arylthiolate concentration. This implies that the rate of decrease in base concentration is equal to twice the rate of *cis*-dichloroethylene consumption. To test this, a comparison was made between the rate of chloride formation (proportional to *cis*-dichloroethylene consumption) and the rate of base consumption. The Mohr method<sup>31</sup> was used for the chloride determination and the results (Table II) demonstrate that the rate of chloride ion formation equals the rate of base consumption.

On the basis of the above considerations, we have followed the kinetics of the reaction by the acid-base method, and have expressed these results in terms of *cis*-dichloroethylene concentration.

The runs were made in 50-ml. volumetric flasks which contained absolute ethanol ("de-oxygenated" by bubbling

TABLE II  
COMPARISON OF METHODS<sup>c</sup>

Run	Concn. sodium ethoxide, mole l. <sup>-1</sup>	Mohr method slope <sup>a</sup> $\times 10^4$	Acid-base method slope <sup>b</sup> $\times 10^4$
A	0.213	12.02	12.64
B	.113	7.55	7.21

<sup>a</sup> Obtained from the plot of  $(-)\log[Cl^-]$  vs. time. <sup>b</sup> Obtained from the plot of  $(-)\log[ArSNa]$  vs. time. <sup>c</sup> Temp.  $57.9 \pm 0.5^\circ$ ; concn. *cis*-dichloroethylene (I), 0.133 mole l.<sup>-1</sup>; concn. sodium *p*-toluenethiolate, 0.20 mole l.<sup>-1</sup>.

with high-purity nitrogen). This precaution was necessary since the arylthiolate is readily oxidized to the disulfide in the presence of oxygen. Sodium ethoxide was standardized against hydrochloric acid using phenolphthalein as the indicator. The arylthiolate solutions were made by dissolving a small amount of *p*-toluenethiol (0.0002 g.) in a volumetric flask containing ethanol and diluting to the mark. *cis*-Dichloroethylene (Matheson) was fractionated through a Todd column packed with glass helices (12.0 mm. inner diameter; 90 cm. length); and a middle cut, b.p.  $59.0^\circ$  (737 mm.),  $n_D^{20}$  1.4481, was used.

The order of addition of reactants was: standard sodium ethoxide solution, standard arylthiol solution and *cis*-dichloroethylene. Zero time was the time of immersion in the constant temperature bath. Aliquots (5.0 ml.) were withdrawn at intervals and immediately quenched in excess hydrochloric acid solution, followed by back titration to the methyl orange end-point with standard sodium hydroxide solution. This end-point was quite sensitive and reproducible.

**Reactions of Chloroacetylene with Sodium *p*-Toluenethiolate.**—Chloroacetylene was generated from its mercury derivative which was prepared by treating *cis*-dichloroethylene with mercuric cyanide and potassium hydroxide<sup>32–34</sup>; the crude product was extracted with chloroform in a Soxhlet unit, m.p.  $173.0$ – $174.0^\circ$  (bath preheated to  $170^\circ$ ).

*Anal.*<sup>35</sup> Calcd. for C<sub>4</sub>Cl<sub>2</sub>Hg: Cl, 22.19. Found: Cl, 21.92.

(30) All boiling and melting points are uncorrected.

(31) H. H. Willard and N. H. Furman, "Elementary Quantitative Analysis," Third Edition, D. Van Nostrand Co., Inc., New York, N. Y., 1940, pp. 178–182.

(32) K. A. Hofmann and H. Kirmreuther, *Ber.*, **42**, 4234 (1909).

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

(34) L. A. Bashford, H. J. Emelús and H. V. A. Briscoe, *ibid.*, 1358 (1938).

(35) Except where noted, all microanalyses were performed by Dr. C. S. Yeh and Mrs. S. L. Margerum, Purdue Chemistry Micro-analytical Laboratory.

A.—Mercuric bis-(chloroacetylde) (10.0 g., 0.031 mole) was decomposed over a one-hour period by adding an aqueous solution (200 ml.) of 4.0 g. (0.0713 mole) of potassium hydroxide and 20.0 g. (0.23 mole) of potassium cyanide, while the generation flask was heated on a steam-cone. The evolved chloroacetylene was carried by a hydrogen stream (the latter was de-oxygenated by passage through Fieser solution<sup>36</sup>) into a reaction flask containing 150 ml. of absolute ethanol. A condenser containing Dry Ice-trichloroethylene was attached to this flask to condense any escaping chloroacetylene. During a 1.5-hour period sodium *p*-toluenethiolate from 7.80 g. (0.0626 mole) of *p*-toluenethiol and 1.435 g. (0.0626 mole) of sodium in 150 ml. of absolute ethanol was added. Including the time of arylthiolate addition, the reaction mixture was heated at reflux for 5 hours. Hydrogen was passed through the cooled reaction mixture to remove any unreacted chloroacetylene. 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. This precaution is necessary since chloroacetylene ignites spontaneously on contact with air, and may detonate. The contents of the trapping tower were filtered and 1.73 g. (17.3% of mercuric bis-(chloroacetylde) was recovered. The reaction mixture was filtered through a sintered-glass funnel, and the residue was washed with hot absolute ethanol; weight of sodium chloride, 0.87 g. The filtrate was concentrated, diluted with water, extracted several times with petroleum ether (30–60°), the extracts dried over magnesium sulfate, evaporated and recrystallized from absolute ethanol to give 4.46 g. (52.2% conversion, 77.4% yield to V) of a product, m.p. 89.5–90.5°. This product did not depress the melting point of an authentic sample of *cis*-1,2-bis-(*p*-tolylmercapto)-ethene (V), m.p. 91.0°. A residual oil, wt. 1.59 g., was fractionally distilled; b.p. 99.0–102.0° (2.2 mm.),  $n_D^{20}$  1.5901, wt. 1.22 g. (13.7% conversion, 20.3% yield to III). The infrared spectrum of this liquid showed the following absorption bands and intensities (0.02 mm. thickness)<sup>37</sup>: 3.35(m), 3.46(m), 5.27(w), 5.61(w), 5.77(w), 6.10(w), 6.27(m), 6.39(m), 6.69(s), 6.92(m), 7.14(m), 7.26(w), 7.78(s), 8.26(w), 8.41(w), 8.96(w), 9.14(m), 9.27(m), 9.63(w), 9.83(m), 11.25(w), 11.97(s), 12.43(s), 12.88(m), 13.12(m) and 15.10(s)  $\mu$ . Both the absorption bands at 7.78(s)  $\mu$ <sup>38</sup> and 15.10(s)  $\mu$  appear to be characteristic for the *cis*-configuration in this series, since these same bands are absent in the spectrum of the *trans* isomer.<sup>12</sup>

The sulfone was prepared by treating 0.30 g. (0.00138 mole) of this liquid with 2.0 ml. (0.0175 mole) of 30% hydrogen peroxide in 30 ml. of glacial acetic acid. The reactants were heated on a steam-bath for one hour, and the contents poured onto ice to give a crude product (wt. 0.35 g., 99.0% yield), which was recrystallized from absolute ethanol and melted at 38.0–39.0° (wt. 0.30 g., 85.0%). Further recrystallization from ethanol increased the melting point to 39.0–40.0°.

*Anal.* Calcd. for C<sub>9</sub>H<sub>9</sub>SO<sub>2</sub>Cl: C, 49.84; H, 4.19; Cl, 16.36. Found: C, 50.17; H, 4.80; Cl, 16.00.

When this *cis*-sulfone (m.p. 39.0–40.0°) was mixed with an authentic sample of *trans*-1-chloro-2-(*p*-tolylsulfonyl)-ethene,<sup>12</sup> (m.p. 46.5–47.0°), by dissolving 0.05 g. of each isomer in 20 ml. of absolute ethanol, followed by evaporation to dryness, only a liquid was obtained which could not be crystallized.

The remainder of the reaction mixture was acidified with concd. hydrochloric acid, extracted with petroleum ether (30–60°), dried over magnesium sulfate and evaporated to give a solid, m.p. 41.0–42.0° (wt. 2.54 g., 32.6% recovery of *p*-toluenethiol).

B.—In order to study the effect of base concentration, II was again treated with *p*-toluenethiol but with one-half the amount of sodium used in the previous experiments:

Mercuric bis-(chloroacetylde) (12.0 g., 0.0383 mole) was decomposed over a 1.5-hour period by the dropwise addition of a solution of 20.0 g. (0.23 mole) of potassium cyanide and 4.0 g. (0.0713 mole) of potassium hydroxide in 200 ml. of water. The chloroacetylene thus evolved was carried by a

hydrogen stream into a reaction flask containing 350 ml. of absolute ethanol, and to which a solution made from 7.80 g. (0.0626 mole) of *p*-toluenethiol and 0.718 g. (0.0313 mole) of sodium in 200 ml. of absolute ethanol was added dropwise over a 1.5-hour period. After heating the reaction mixture for 4 hours (including time of arylthiolate addition), and subsequent cooling, hydrogen was passed through for an additional 2 hours.

Mercuric bis-(chloroacetylde) was filtered from the trapping tower (charged with 4.6 g. (0.082 mole) of potassium hydroxide and 10.0 g. (0.0397 mole) of mercuric cyanide in 50 ml. of water), washed with distilled water and dried; wt. 2.35 g. (19.6% recovery).

Sodium chloride (wt. 0.30 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 dried over magnesium sulfate and recrystallized from 95% ethanol to give 4.23 g. (49.2% yield) of *cis*-1,2-bis-(*p*-tolylmercapto)-ethene (V), m.p. 90.0–90.5°. Since the remainder of the alcohol solution could not be further crystallized, it was diluted with water, extracted with petroleum ether (30–60°), the extracts dried over magnesium sulfate and evaporated to give 6.5 g. of a liquid which was fractionally distilled: cut I, b.p. 79.0° (1.0 mm.),  $n_D^{20}$  1.5890, wt. 2.65 g.; cut II, b.p. 91.5–94.5° (1.3 mm.),  $n_D^{20}$  1.5923, wt. 2.85 g. The infrared spectra of both fractions were identical with the spectrum of *cis*-1-chloro-2-(*p*-tolylmercapto)-ethene (III), which had been previously prepared from a similar reaction.

In addition, cut I had two infrared absorption bands characteristic of a monosubstituted acetylene (3.08  $\mu$ ) and an acetylenic bond (4.90  $\mu$ )<sup>38,39</sup> which were also present in the infrared spectrum of authentic *p*-tolylmercaptoacetylene (IV).<sup>38</sup> Like intermediate IV, cut I turned dark on standing.

Since no *p*-toluenethiol was recovered from the acidified reaction mixture, the total yield of *cis*-1-chloro-2-(*p*-tolylmercapto)-ethene (III) was 47.4% (5.50 g.).

Cut I (0.50 g., 0.0027 mole) in 15 ml. of 95% ethanol was treated with 4.54 ml. (0.00675 equivalent) of mercuric iodide reagent,<sup>39</sup> the chilled (0°) mixture was stirred for several minutes, filtered and washed with chilled 50% ethanol to give 0.42 g. (62.8% yield) of a solid which was recrystallized from 95% ethanol (Norite A), m.p. 143.5–144.5°. A mixed melting point determination with an authentic sample of mercuric bis-(*p*-tolylmercaptoacetylde)<sup>38</sup> showed no depression (m.p. 144.0–145.0°). Cut II (0.10 g., 0.00054 mole) was treated likewise with 2.25 ml. (0.00333 equivalent) of mercuric iodide reagent to give 0.07 g. (52.3% yield) of a solid, m.p. 144.0–145.0°, following recrystallization from 95% ethanol (Norite A).

**Reaction of *cis*-1-Chloro-2-(*p*-tolylmercapto)-ethene with Sodium *p*-Toluenethiolate. A. Presence of Sodium Ethoxide.**—The following mixture was heated to reflux under a nitrogen atmosphere for 24 hours: *cis*-1-chloro-2-(*p*-tolylmercapto)-ethene (0.20 g., 0.00097 mole), *p*-toluenethiol (0.114 g., 0.00097 mole), sodium (0.03 g., 0.0011 mole) in 30 ml. of absolute ethanol. Sodium chloride (wt. 0.04 g.) was filtered off and washed with hot absolute ethanol. The filtrate was concentrated, diluted with water and extracted with petroleum ether. The residue obtained after evaporating the petroleum ether was recrystallized from 95% ethanol to give a solid, m.p. 89.5–90.5°, wt. 0.26 g. (98.4% yield). No depression was observed with an authentic sample of *cis*-1,2-bis-(*p*-tolylmercaptoethene (V), m.p. 91.5°.

**B. Absence of Sodium Ethoxide.**—A solution of 0.050 g. (0.0027 mole) of *cis*-1-chloro-2-(*p*-tolylmercapto)-ethene, 0.055 g. (0.0024 mole) of sodium and 0.336 g. (0.0027 mole) of *p*-toluenethiol in 30 ml. of absolute ethanol was heated to reflux for 24 hours under a nitrogen atmosphere. No sodium chloride was isolated. The filtrate was concentrated, diluted with water and extracted with petroleum ether (30–60°). The petroleum ether extracts were washed with 50 ml. of 5 *N* potassium hydroxide (to remove *p*-toluenethiol) and then with water. The petroleum ether extracts were dried over magnesium sulfate and evaporated to give an oil, wt. 0.49 g. (98.0% recovery of *cis*-haloolefin).

The remainder of the reaction mixture (including the po-

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

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

(38) W. E. Truce, H. E. Hill and M. M. Boudakian, *THIS JOURNAL*, **78**, 2760 (1956).

(39) J. R. Johnson and W. L. McEwen, *ibid.*, **48**, 469 (1926); J. U. Nef, *Ann.*, **308**, 299 (1899).

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)<sup>8</sup> 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.

**Acknowledgment.**—The authors gratefully acknowledge support of this work by the Office of Ordnance Research, Department of the Army, under Contract No. DA-33-008-ORD-983.

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<sup>1</sup>

RECEIVED OCTOBER 21, 1955

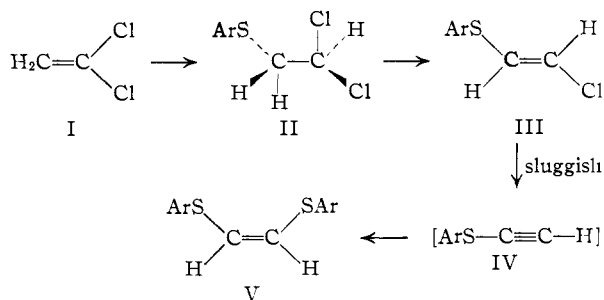
Vinylidene chloride (I) reacts with sodium *p*-toluenethiolate to give exclusively *cis*-1,2-bis-(*p*-tolylmercapto)-ethene (V). Evidence is provided for a mechanism. Depending on the conditions employed, the reaction can be controlled so that 1,1-dichloro-2-(*p*-tolylmercapto)-ethane (II), *trans*-1-chloro-2-(*p*-tolylmercapto)-ethene (III) or V can be isolated. Intermediates II, III and *p*-tolylmercaptoacetylene (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<sup>2,3</sup> and sulfites,<sup>4</sup> 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-ethane-trisulfonate.<sup>4</sup> 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.<sup>2</sup>

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,<sup>2,3</sup> an elimination-addition mechanism seemed probable. However, FitzGibbon<sup>5</sup> found that vinylidene chloride did not react with alkaline mercuric cyanide; in contrast, *cis*-dichloroethylene gave mercuric bis-(chloroacetylidene), Hg(C≡C—Cl)<sub>2</sub>, under the same conditions. Attempts in this laboratory to prepare mercuric bis-(chloroacetylidene) 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<sup>6–10</sup> may be explained as due to a polarizing influence (inductive effect) of the chlorine atoms on an in-<sup>(-)</sup>ipient carbanion, ArS<sup>(-)</sup>CH<sub>2</sub>C(Cl)<sub>2</sub>, 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

(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).

(4) W. E. Truce and M. M. Boudakian, *ibid.*, **78**, 2752 (1956).

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

(6) O. R. Quayle and E. E. Royals, *THIS JOURNAL*, **64**, 226 (1942).

(7) J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 297 (1951).

(8) P. B. D. de la Mare and C. A. Vernon, *J. Chem. Soc.*, 3331 (1952).

(9) J. Hine and W. H. Brader, Jr., *THIS JOURNAL*, **75**, 3964 (1953).

(10) J. F. Bunnett and G. T. Davis, *ibid.*, **76**, 3011 (1954).