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The Free Radical Addition of Thiolacetic Acid and of Hydrogen Bromide to *cis*- and *trans*-2-Chloro-2-butene[1]

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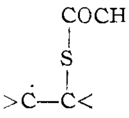
The light-initiated, free-radical addition of thiolacetic acid to either *cis*- or *trans*-2-chloro-2-butene at −78° gave the same mixture of about 90% *threo*- and 10% *erythro*-2-acetylmercapto-3-chlorobutane. This is strong evidence against the existence of a bridged radical intermediate. With ultraviolet irradiation, hydrogen bromide in pentane solution rapidly isomerized the starting olefins, even at −78°. At room temperature and above, thiolacetic acid also gave isomerization indicating the ease of reversibility of the first step of these radical addition reactions.

A report of the stereospecific radical *trans* addition of hydrogen bromide to *cis*- and *trans*-2-bromo-2-butene[3] and of the stereospecific *trans* addition of hydrogen bromide to 1-bromo- and 1-methylcyclohexenes,[4] which were interpreted[3,4] in terms of a three-membered bridged radical intermediate, prompted us to investigate the stereospecificity of the addition of thiolacetic acid to *cis*- and *trans*-2-chloro-2-butene. Since this work was initiated, the postulate of bridged radicals has been made much less attractive by observations that: (1) radical addition of $BrCCl_3$,[5a] $C_6H_5SO_2I$[5b] to *cis*- and *trans*-2-butenes are not stereospecific, but rather give the same mixture of products; (2) radical additions of divalent sulfur to 1-halo-[6a] and 1-alkylcyclohexenes[6b] are only partially stereospecific; (3) addition of peroxy radicals to indene is not stereospecific[7]; and (4) when radical rearrangement occurs the ratio of unrearranged to rearranged product changes with concentration, which is consistent with separate radicals, but not with a single bridged species.[8] The CH_3COS group offers unusual opportunities for bridging since structures with three-, four- or five-membered rings (B,C,D) are possible for the initially-formed adduct A. However, the present investigation indicates that bridged intermediates of this type play little or no part in determining the products of the reaction.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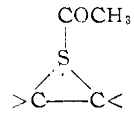
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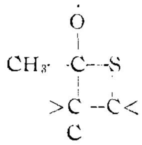
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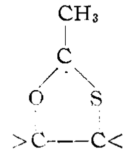
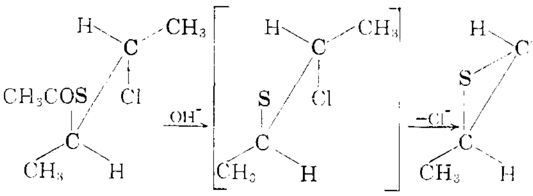

D

Stereospecific *trans* addition of thiolacetic acid to *cis*-2-chloro-2-butene (Ia) should lead to *dl*-*erythro*-2-acetylmercapto-3-chlorobutane (IIa), as shown, and *trans* addition to *trans*-2-chloro-2-butene (Ib) should lead to the *threo* isomer IIb.

I a II a

Alkaline hydrolysis[9] of the *erythro* isomer should give *trans*-2-butene episulfide (IIIa), since the episulfide formation occurs by a mechanism similar to the formation of *cis*- and *trans*-2-butene epoxides from the diastereoisomeric chlorohydrins, a reaction which has been shown to be stereospecific.[10]



IIa IIIa

The reaction of the episulfide IIIa with phenyllithium has been shown to be stereospecific,[11] giving lithium thiophenoxide and *trans*-2-butene. Similarly, *cis*-2-butene episulfide (IIIb) reacts with phenyllithium to give *cis*-2-butene. The relative amounts of *threo* and *erythro* adducts (IIa and IIb) formed in the reaction of thiolacetic acid with Ia or Ib can be determined, therefore, by (1) alkaline hydrolysis to the episulfides, (2) treatment of these with phenyllithium, and (3) infrared analysis of the 2-butenes obtained. The percentage of *cis*-2-butene will represent the amount of *threo* adduct IIa present in a mixture of IIa and IIb, and the amount of *trans*-2-butene will correspond to the amount of *erythro* isomer.

Addition of thiolacetic acid to either *cis*- or *trans*-2-chloro-2-butene at ordinary temperatures (25–80°) with light and *t*-butyl hydroperoxide initiation[12] was found to give essentially the same

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[1] Presented at the Miami Meeting of the American Chemical Society, April, 1957, see p. 10-O of Abstracts.

[2] Research and Development Division, Humble Oil & Refining Co., Baytown, Tex. American Petroleum Institute (Project 48B) Fellow, 1954–1955, 1956–1957, Northwestern University.

[3] M. E. Epstein, Ph.D. Dissertation, Syracuse University, 1951.

[4] H. L. Goering, P. L. Abell and B. F. Aycock, THIS JOURNAL, **74**, 3588 (1952).

[5] (a) P. S. Skell and R. C. Woodworth, *ibid.*, **77**, 4638 (1955); (b) P. S. Skell and J. H. McNamara, *ibid.*, **79**, 85 (1957); (c) P. S. Skell, R. C. Woodworth and J. H. McNamara, *ibid.*, **79**, 1253 (1957).

[6] (a) H. L. Goering, D. I. Relyea and D. W. Larsen, *ibid.*, **74**, 348 (1956); (b) F. G. Bordwell and W. A. Hewett, *ibid.*, **79**, 3493 (1957). The first report of lack of stereospecificity was made by the latter authors in 1954 (p. 6-O Abstracts, A.C.S. Meeting, New York, Sept., 1954).

[7] G. A. Russell, THIS JOURNAL, **78**, 1035 (1956).

[8] S. J. Cristol, G. D. Brindell and J. A. Reeder, *ibid.*, **80**, 635 (1958).

[9] Addition of thiolacetic acid to haloalkenes followed by hydrolysis is a general procedure for preparing cyclic sulfides; see F. G. Bordwell and W. A. Hewett, *J. Org. Chem.*, **23**, 636 (1956).

[10] C. E. Wilson and H. J. Lucas, THIS JOURNAL, **58**, 2396 (1936).

[11] N. P. Neureiter and F. G. Bordwell, *ibid.*, **81**, 578 (1959).

[12] With these olefins and a 100-watt bulb as a light source it was advantageous to use a few drops of *t*-butyl hydroperoxide to accelerate the reaction. In the additions at −78° the use of hydroperoxide was unnecessary because of the much more effective lamp employed.

mixture of *threo*- and *erythro*-thiolacetates (about 75% *threo* and 25% *erythro*). Examination of the recovered, unreacted olefin in each instance, however, showed that isomerization of the 2-chloro-2-butene to essentially the equilibrium mixture (about 80% *trans*) had occurred. A product mixture containing similar proportions of *threo*- and *erythro*-thiolacetates was obtained from the addition of thiolacetic acid to an equilibrium mixture of *cis*- and *trans*-2-chloro-2-butenes. A study was next made to determine the conditions for isomerization. Isomerization of the *cis*- and *trans*-2-chloro-2-butenes is readily detected, since each possesses two characteristic infrared bands, 12.15 and 14.9 μ for *cis*- and 7.8 and 12.5 μ for *trans*-2-chloro-2-butene.

Refluxing either *cis*- or *trans*-2-chloro-2-butene (b.p. 69° and 62°, respectively) with *t*-butyl hydroperoxide for 5–7 hours caused little or no isomerization. Refluxing either olefin in the presence of 25 mole per cent. of chloroacetic acid, an acid of somewhat greater strength than thiolacetic acid, also failed to give isomerization. Similarly, *cis*-olefin in the presence of a little gaseous hydrogen chloride failed to isomerize on refluxing. Irradiation of either *cis*- or *trans*-olefin with ultraviolet light for periods up to 7 hours caused yellowing of the sample, but only a few per cent. of isomerization (3–8%).

A sample of 1.7 g. of *cis*-2-chloro-2-butene was treated with *two drops* of thiolacetic acid and the solution was irradiated for 30 minutes. At the end of this period, 68% of *trans*-olefin and 32% of *cis*- olefin were present, which indicates about 85% isomerization. Addition of two more drops of thiolacetic acid and irradiation for 70 minutes longer brought the percentage of *cis*-olefin in the mixture to nearly the equilibrium value (24% *vs.* 20%). Isomerization of *cis*- and *trans*-4-methyl-2-pentenes with thiolacetic acid and light was also demonstrated.[13]

By carrying out the reaction at −78° with strong internal ultraviolet irradiation it was found possible to avoid isomerization of the olefins. However, addition of thiolacetic acid to individual samples of *cis*- and *trans*-2-chloro-2-butenes still gave mixtures containing essentially the same relative proportions of *threo*- and *erythro*-thiolacetates, as indicated by the identity of their refractive indices and infrared spectra. Reaction of the thiolacetates with aqueous potassium hydroxide gave episulfide mixtures which also had identical refractive indices and infrared spectra. Reaction of the episulfide mixtures with phenyllithium gave, in each instance, essentially the same mixture of butenes, containing about 10% of *trans*- and 90% of *cis*-2-butene.

The isomerization experiments show that at room temperature each molecule of thiolacetic acid is capable of isomerizing a very large number of olefin molecules. This suggests that addition of the $CH_3COS\cdot$ radical is readily reversible.[14] But in the present system, lowering the temperature to −78° evidently retards the rate of the reverse reaction more than that of the hydrogen atom abstraction step, and isomerization does not occur.

The failure of the individual olefins to give different products in their additions shows that the bridged structures (B,C,D) provide little, if any, stabilizing influence for the intermediate radical. The bridged three-membered ring structure B, which is analogous to the well-supported bromonium[15] and sulfonium[16] ion intermediates in ionic additions, would require overlap between the sp^3 orbital of carbon[17] and a *d* orbital of the sulfur atom. The accumulating evidence indicates that divalent sulfur bonds utilizing *d*-orbitals are very weak unless there is a high electron density (radical or carbanion) on an *adjacent* atom.[18]

The formation of similar mixtures from both *cis*- and *trans*-2-chloro-2-butene under non-isomerizing conditions means that the same radical intermediate is formed from each olefin. The situation is similar to that observed for the addition of the $\cdot CCl_3$ radical to *cis*- and *trans*-2-butene.[5a] Six different non-eclipsed rotational conformations are possible for the intermediate, if the radical center is assumed to be pyramidal and capable of undergoing inversion. Since the activation energy of the hydrogen abstraction step is low,[13] the transition state for hydrogen abstraction may be said to resemble the intermediate rather closely.[19] One of the conformations then approximates the transition state of lowest energy for the hydrogen transfer reaction leading to formation of the predominant *threo* product.

At higher temperatures the mixtures from either *cis*- or *trans*-2-chloro-2-butene (though accompanied by isomerization of the olefins) were still identical, but now contained a larger proportion of the *erythro* adduct (about 10% *erythro* at −78°, about 15% at −20°, and 25–30% at 25–85°).

Addition of hydrogen bromide to *trans*- and *cis*-2-chloro-2-butene was investigated in pentane solution at −20°, using an ultraviolet light source to initiate the reaction, and at 25–30° in hexane solution containing benzoyl peroxide. In all instances approximately the same mixture of diastereoisomeric 2-bromo-3-chlorobutanes was formed (about 70% *threo* and 30% *erythro*). Analysis of the mixture was accomplished in two ways: (1) treatment with alcoholic potassium hydroxide to form a mixture of *cis*-2-chloro-2-butene (from the *erythro* adduct) and *trans*-2-chloro-2-butene (from the *threo* adduct), and (2) treatment with zinc dust in distilled water[20] at room temperature to form a mixture of *cis*- and *trans*-2-

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(13) Rapid isomerization of *cis*-2-butene by methanethiol at 60° has been observed by C. Walling and W. Helmreich, This Journal, **81**, 1144 (1959).

(14) C. Sivertz, W. Andrews, W. Elsdon and K. Graham, *J. Polymer Sci.*, **19**, 587 (1956), have concluded that such additions are reversible in the gas phase, and C. Walling (ref. 13) has recognized that this may also occur in solution.

(15) I. Roberts and G. E. Kimball, This Journal, **59**, 947 (1937).

(16) A. J. Havlik and N. Kharasch, *ibid.*, **77**, 1150 (1955), and earlier papers.

(17) The radical is assumed in this discussion to have a tetrahedral rather than a planar structure; see ref. 5 for an excellent discussion of this point.

(18) See F. G. Bordwell and P. J. Boutan, This Journal, **78**, 854 (1956).

(19) G. S. Hammond, *ibid.*, **77**, 334 (1955).

(20) W. M. Schubert, B. S. Rabinovitch, N. R. Larson and V. A. Sims, *ibid.*, **74**, 4590 (1952).

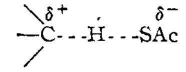
butenes in a ratio corresponding to the relative percentages of *threo*- and *erythro*-dihalobutanes, respectively, which were present in the adduct mixture. The resulting olefin mixtures were analyzed by infrared. Agreement between the two methods was good. However, if the dehalogenation with zinc was carried out in the presence of ethanol, or if the zinc-copper couple described for such reactions[21] was used, or if the temperature rose much above 25°, a decrease of stereoselectivity in the elimination was observed.

Complete equilibration of *trans*- and *cis*-2-chloro-2-butenes to a mixture containing about 80% *trans* and 20% *cis* was realized within a few minutes when hydrogen bromide was passed into irradiated pentane solutions of either of the olefin isomers at 25°, −20° and −78°. It is apparent that under these conditions, equilibration precedes addition.[22] However, despite the equilibration of the starting olefins with hydrogen bromide, and the equilibration of the radical intermediates in the thiolacetic acid additions, it should be pointed out that the additions are stereoselective, leading to 70 and 90% respectively, of the preferred diastereoisomeric adduct.

Since this work was completed four additional examples have been found of stereoselective free radical reactions in acyclic systems where the stereochemistry of the products is known. Thiolacetic acid with 2-bromo-2-butene (25-80°) gives a mixture of the *threo* and *erythro* adducts in a ratio of from 2.5-3.0 to 1.[23] Goering and Larsen have found that free radical addition of hydrogen bromide to either of the 2-bromo-2-butenes at 25° gives the same mixture of about 75% *dl*- and 25% *meso*-2,3-dibromobutane.[24] However, Fredricks and Tedder find in the gas-phase chlorination of 2-chlorobutane at 35° that *meso*- and *dl*-2,3-dichlorobutane are formed in the ratio of 2.5 to 1.[25] Finally, Greene, Remers and Wilson report formation of more than 90% of *meso*-stilbene dibromide from the reaction of either bibenzyl or α-bromobibenzyl with N-bromosuccinimide.[26]

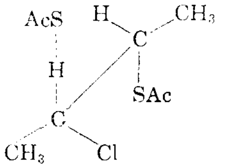
In each case the intermediate radical has reacted preferentially *via* one of two[27] competing transition states for the final transfer step. The difference in activation energies (except in the stilbene dibromide system) is less than 1 kcal./mole.

The most satisfying explanation of the observed stereochemistry is perhaps to be found in the polar character of the transfer reaction. Greene, Remers and Wilson[26] have pointed out that the negative ρ-values observed in radical reactions at the benzyl positions of *p*-substituted toluenes indicate considerable ionic character in the transition state, in which the negative end of the dipole is directed away from the site of attack. Extension to the transfer step in the addition of thiolacetic acid gives a situation as in IV. If such a dipole development is occurring in the transition state, it is clear that this dipole should be preferentially oriented *away* from the largest permanent (negative) dipole on the saturated carbon. This can be realized only if the molecule engaging in transfer preferentially approaches the radical center *trans* to the most negative group on the saturated carbon.



IV

At the same time, steric interactions should be minimized. With the larger substituent on the radical carbon in the larger remaining steric "hole" afforded by the groups on the saturated carbon. the energy of activation to the transition state can be further reduced. In V the CH_3 lies between the SAc and the H, while the smaller Cl occupies the smaller "hole" between the CH_3 and the SAc. Such a transition state gives the *threo* product.



V

The application of this polar-steric scheme to the above examples predicts in each instance the predominant product—even to the *meso*-2,3-dichlorobutane and the *meso*-stilbene dibromide. The order of "steric" size required is Ph > SAc > CH_3 > Br ≥ Cl > H.

Experimental[28]

cis- and *trans*-**2-Chloro-2-butenes.**—Chlorination of pure *cis*- and *trans*-2-butene (Phillips, 99% pure grade), according to Hoff, Greenlee and Boord,[29] gave the pure *dl*- (b.p. 116-117.2°, $n^{25.2}D$ 1.4399) and *meso*- (b.p. 113-113.7°, $n^{25.1}D$ 1.4384) 2,3-dichlorobutanes. A modification of the dehydrohalogenation procedure of the same authors[29] gave 75% yields of the pure 2-chloroölefins. Ethanol was used as the solvent and refluxing was continued for 18 to 24 hours after addition of the dihalide. The mixture was distilled until the vapor temperature reached 78°, the distillate was washed with ice-water, clarified with 50% glycerol, dried over anhydrous sodium sulfate and distilled through a helices-packed column in the presence of a little sodium bicarbonate. The *cis*-2-chloro-2-butene had b.p. 69-70°, $n^{25}D$ 1.4209 and strong characteristic infrared peaks at 14.9 and 12.15 μ. The *trans*-2-chloro-2-butene had b.p. 62.0-62.2°, $n^{25}D$ 1.4158, and strong characteristic infrared bands at 7.8 and 12.5 μ. These physical constants suggest a purity for the *cis* isomer greater than that reported in the literature.[30]

In later experiments it was found possible to separate the two isomers from a mixture obtained by chlorinating and dehydrochlorinating a commercial mixture of *cis*- and *trans*-2-butenes. One pass through a 2 × 70 cm. glass helices-

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[21] W. G. Young and S. Winstein, This Journal, **58**, 102 (1936).

[22] Since this work was completed stereospecific *trans* addition of hydrogen bromide to *cis*- and *trans*-2-bromo-2-butene has been reported under somewhat different conditions, see H. L. Goering and D. W. Larsen, *ibid.*, **79**, 2653 (1957).

[23] N. P. Neureiter, unpublished work.

[24] H. L. Goering and D. W. Larsen, This Journal, **81**, 5937 (1959).

[25] P. S. Fredricks and J. M. Tedder, *Proc. Chem. Soc.*, **9** (1959).

[26] F. D. Greene, W. A. Remers and J. W. Wilson, This Journal, **79**, 1416 (1957).

[27] Though there are six possible approximatable transition states for the transfer reaction (*vide supra*), there are only two distinct groups of three stereochemically equivalent paths. For convenience we shall speak of only two competing transition states—one leading to the *threo* (or *dl*) and the other to the *erythro* (or *meso*) product.

[28] All boiling points and melting points are uncorrected.

[29] M. C. Hoff, K. W. Greenlee and C. F. Boord, This Journal, **73**, 3329 (1951).

[30] (a) L. Waves, *Bull. soc. chim. Belg.*, **39**, 435 (1930); (b) A. Petrov and A. Sapozhnikova, *Zhur. Obsch. Khim.*, **7**, 476 (1937).

packed column at a 20-to-1 reflux ratio gave samples of both *trans* (95% pure) and *cis* (99% pure) isomers.

Mixtures of the two isomers were analyzed by infrared spectroscopy utilizing the 14.9 (*cis*) and 7.8 (*trans*) μ bands. The spectra were run on a Baird Associates infrared spectrometer equipped with rock salt optics. Extinction coefficients at the wave lengths in question were determined in a single cell for both the pure isomers. Agreement with Beer's law was assumed over the concentration ranges involved. Analyses were estimated to be accurate to only ±5% absolute, but within ±2% relative to one another.

Addition of Thiolacetic Acid to 2-Chloro-2-butene at 25°.—A mixture of the chlorobutene and acid (0.142 mole) was illuminated with a 100-watt bulb located 2 cm. away from the flask, and 20 drops of commercial *t*-butyl hydroperoxide (Lucidol Corp.) was added at once through the top of the condenser. The reaction mixture was let stand with occasional shaking for 1 hr., though vigorous heat evolution was usually observed after 5–10 min. The maximum internal temperature of the reaction mixture was 89°. Subsequent distillation of the mixture at the water-pump gave 66–78% of the theoretical yield of 1:1 adduct, b.p. 80–84° (13 mm.), from both *cis*- and *trans*-2-chloro-2-butene.

Isomerization of 2-Chloro-2-butene.—*trans*-2-Chloro-2-butene (15 g., 0.164 mole) and thiolacetic acid (4.6 g., 0.061 mole) were allowed to react under the conditions described above. After 40 min. the mixture was distilled at atmospheric pressure. The distillate (10.1 g., b.p. 62–62°) was washed with 10% potassium hydroxide solution and with water, clarified with 50% glycerol, dried over anhydrous sodium sulfate and sodium carbonate and distilled in the presence of a little sodium bicarbonate. The product was a mixture of *cis*- and *trans*-2-chloro-2-butene. Its infrared spectrum indicated it to be 20% *cis*.

The isomerization experiment was repeated using the *cis* compound (7.5 g.) and thiolacetic acid (2.1 g.). A total of 4.3 g. of unreacted compound was recovered; its in-infrared spectrum showed it to be 20% *cis*-2-chloro-2-butene.

A 5-cc. sample of the *trans*-chlorobutene was refluxed with 15 drops of *t*-butyl hydroperoxide for 5 hr. Infrared analysis showed that less than 1% isomerization had occurred.

A 4.0-g. sample of *cis*-chlorobutene was refluxed with 50 drops of *t*-butyl hydroperoxide for 2 hr. No isomerization was detectable.

A sample of the *trans* isomer was irradiated for 7 hr. in a Pyrex tube with a Hanovia type 16200 ultraviolet lamp. Less than 3% isomerization was observed.

A sample of the *trans* isomer irradiated in a quartz vessel for 5 hr. with the Hanovia ultraviolet lamp showed less than 3% isomerization.

A sample of *cis*-chlorobutene in a quartz vessel was irradiated for 6.5 hr. with a Hanovia ultraviolet lamp. Yellowing of the material and 7–8% isomerization were observed.

A sample of *trans*-chlorobutene was refluxed for 50 min. with chloroacetic acid (0.25 equivalent). No isomerization of the recovered chlorobutene was detectable.

Refluxing 4.0 g. of *cis*-chlorobutene with 1.3 g. of chloroacetic acid for 1 hr. produced no detectable isomerization of the chlorobutene.

Hydrogen chloride gas was bubbled through a sample of *cis*-chlorobutene for several minutes followed by refluxing for 2 hr. No isomerization of the chlorobutene was detectable.

A mixture of 8.1 g. of *trans*-chlorobutene and 8 drops of thiolacetic acid was irradiated with the Hanovia ultraviolet lamp for 30 min. The infrared spectrum showed 7% of the *cis* isomer present in the mixture. Sixteen more drops of thiolacetic acid was added and irradiation continued for an additional 70 min. A infrared spectrum of the mixture showed the presence of 20% of the *cis*-chlorobutene.

A mixture of 1.7 g. of *cis*-chlorobutene and 2 drops of thiolacetic acid was irradiated for 20 min. with the ultraviolet lamp. There was still 29% of the *cis* isomer left. Two more drops of thiolacetic acid was added and irradiation was continued for an additional 30 min. The mixture now contained 22% of the *cis*-chlorobutene.

Addition of Thiolacetic Acid to *trans*-2-Chloro-2-butene at −78°.—The apparatus was similar to that described by Goering, Relyea and Larsen,[8a] and provided high intensity internal illumination of the reactants. In a test run at −20° a yield of 92% of the 1:1 adduct was obtained without the use of the hydroperoxide catalyst. To prevent warming of the reaction mixture by the lamp, a stream of cooled, partially dried air was circulated continuously between the discharge coils and the quartz walls of the lamp.

The sample of *trans*-2-chloro-2-butene (14.0 g., 0.155 mole) containing 5% of the *cis*-isomer was placed in the reaction vessel and cooled to −70°, while a calcium chloride tube topped the sidearm of the reaction flask to prevent moisture condensation. Thiolacetic acid (9.4 g., 0.124 mole) was added rapidly, the reactants were mixed by shaking, the lamp was inserted into the reaction flask, the flask was surrounded with a Dry Ice and acetone cooling mixture and irradiation was begun. After 50 min. irradiation was discontinued and about 5 g. of sodium bicarbonate and a few cc. of water were added to the reaction mixture while still cold; in a preliminary experiment some post-reaction isomerization had been observed during the processing. The mixture was let warm to room temperature, more water was added, the aqueous layer was saturated with sodium sulfate to float the organic product and the layers were separated. The organic layer was washed several times with water, dried over anhydrous magnesium sulfate in the presence of a little sodium carbonate and distilled through a short Vigreux column at the water-pump. A total of 2.4 g. of unreacted chlorobutene was collected in a Dry Ice trap; its infrared spectrum was essentially identical with that of the starting chlorobutene. From the distillation, 11.7 g. of the adduct was obtained, b.p. 96–98° (27 mm.), $n^{25.3}$D 1.4841. This is a 56.8% yield based on thiolacetic acid. In a second experiment 12.0 g. of material was obtained, b.p. 97–100° (30 mm.), $n^{29.7}$D 1.4823.

Addition of Thiolacetic Acid to *cis*-2-Chloro-2-butene at −78°.—The experiment was carried out exactly as with the *trans* isomer described above. During the processing, however, it was necessary to add a little pentane to the organic product to separate it from the aqueous layer. After washing and drying, the pentane was removed under a 19-cm. Vigreux column, after which the product was distilled as before. In the Dry Ice trap was collected 4.0 g. of material containing unreacted chlorobutene contaminated with a little pentane. The presence of the pentane did not affect the infrared analysis, which showed less than 3% isomerization of the starting material. A total of 12.0 g. of adduct was obtained, b.p. 96–99° (28 mm.), $n^{29.8}$D 1.4821. This is a 58.2% yield based on thiolacetic acid. The infrared spectrum of the adduct was identical with that of the adduct obtained from the *trans* isomer.

Alkaline Conversion of Adducts to Episulfides.—The adduct mixture (11.5 g., 0.0691 mole) was added to a solution of 0.168 mole of potassium hydroxide in 185 cc. of water (0.91 *M*). Vigorous stirring was begun and the mixture was heated to 43°. This temperature facilitated the hydrolysis without causing subsequent reaction of the episulfides. The heat of reaction was sufficent to maintain this temperature. When the temperature dropped below 40° (40 to 50 min.) the reaction was considered essentially complete. The course of the hydrolysis could be followed by observing the formation of the lighter-than-water episulfide layer and the disappearance of the heavy thiolacetate layer. At the end of the reaction the organic layer was separated, the product was dried over anhydrous sodium sulfate and distilled through a 4-inch Vigreux column. The yield was lowered by taking the product up in pentane. It seemed likely that a pentane–episulfide azeotrope was formed. From the adduct of the *cis*-chlorobutene a yield of 3.8 g. (63%) was obtained, b.p. 49–51° (125 mm.), $n^{25.2}$D 1.4739. From the adduct of the *trans*-chlorobutene was formed 3.6 g. (59%) of material, b.p. 51–54° (135 mm.), $n^{25.2}$D 1.4740. Between 1 and 2 g. of high boiling material, assumed to be unhydrolyzed thiolacetate, was left in the distilling flask in both runs. The infrared spectrum of the episulfide mixture obtained from the *cis*-chlorobutene was identical with the spectrum of the episulfide mixture obtained from the *trans*-chlorobutene. From the infrared spectrum both mixtures were estimated to contain approximately 10% of the *trans*-2-butene episulfide. The characteristic infrared bands for the two isomers, as well as a better method for analyzing mixtures of them, are given in the literature.[11]

Reaction of Episulfide Mixtures with Phenyllithium.—The apparatus consisted of a flask equipped with a stirrer and a small dropping funnel inserted in a sidearm. A short distilling column which could be cooled with ice-water topped the flask. From the top of the column a delivery tube conducted the gaseous products through a bubbler trap filled with 40% sulfuric acid into a brine-filled azotometer. The gas could be introduced into a small vacuum line with provisions for freezing out the product with liquid nitrogen, pumping off any air present, vaporizing the product into an infrared cell and measuring the pressure.

Prior to a run, the system was thoroughly flushed with dry nitrogen. An ether solution containing a 100 to 150% excess of phenyllithium was placed in the reaction flask and vigorously stirred during dropwise addition of the episulfide dissolved in a little ether; the latter was forced through the dropping funnel with a slight head of nitrogen pressure. Gas evolution began almost immediately and continued throughout the addition. Stirring was continued for 0.5 to 1 hr. after addition was completed. The ether solution was then boiled gently for 1 or 2 min. to remove any dissolved butene, and the gaseous products flushed completely into the azotometer tube with a stream of dry nitrogen.

The mixtures of *cis*- and *trans*-2-butenes were analyzed by infrared spectroscopy. Contamination of the products with ethyl ether and ethylene complicated the infrared analysis, but the optical density at 14.85 μ was used for *cis*-2-butene, the ethyl ether concentration estimated from the optical density at 8.81 μ, ethylene at 70.5 μ and the *trans*-2-butene determined by differences. At best, the accuracy on those analyses was ±5% absolute; however, it was clear that the product mixtures from the *cis*- and *trans*-2-chloro-2-butenes were essentially identical in composition. The mixture from *trans*-2-chloro-2-butene was calculated to contain 8% *trans*-2-butene; the mixture from *cis*-2-chloro-2-butene to be 7% *trans*-2-butene.

Addition of Hydrogen Bromide to 2-Chloro-2-butene.—The method was adapted from that of Goering, Abell and Aycock.[4] Anhydrous hydrogen bromide was bubbled into a solution of *cis*-2-chloro-2-butene (16.0 g., 0.177 mole) in 160 cc. of dry, olefin-free pentane contained in a quartz flask cooled to −20° and irradiated at close range with a Hanovia type 16200 ultraviolet lamp. Stirring with a magnetic stirrer was continued until hydrogen bromide was no longer absorbed (about 30 min.). The mixture was washed with sodium bicarbonate solution and with water, and dried over anhydrous sodium sulfate. Solvent removal and distillation afforded 26.7 g. (88%) of material, b.p. 63–64° (60 mm.), $n^{25.2}$D 1.4740. A repetition of this procedure with a mixture of 95% *trans*- and 5% *cis*-2-chloro-2-butene gave an 81% yield of adduct, b.p. 63–64° (60 mm.), $n^{25.5}$D 1.4740.

Addition of Hydrogen Bromide to *cis*-2-Chloro-2-butene *via* the Method of Epstein.[3]—A mixture of 200 cc. of dry, olefin-free petroleum hexane and 2.4 g. of benzoyl peroxide was treated in the diffuse light of the laboratory, with anhydrous hydrogen bromide at a rate of 0.5 mole per hour. With continuous hydrogen bromide flow and vigorous stirring, *cis*-2-chloro-2-butene (0.169 mole) was added dropwise over a period of 45 min. Stirring and hydrogen bromide addition were continued for another 30 min. The mixture was washed with water, bicarbonate solution and again with water, and then dried over anhydrous magnesium sulfate. Distillation afforded 19.2 g. (66.4%) of colorless liquid, b.p. 62–64° (60 mm.), $n^{25.2}$D 1.4745.

Isomerization of 3-Chloro-2-butene with Hydrogen Bromide.—Anhydrous hydrogen bromide was bubbled into *cis*-2-chloro-2-butene (15.6 g.) dissolved in 100 cc. of dry petroleum pentane contained in a quartz flask cooled to −20° and irradiated at close range with a Hanovia ultraviolet lamp. After 4 min. the hydrogen bromide addition was stopped, the mixture was washed with sodium bicarbonate solution and with water, and dried over anhydrous sodium sulfate. Most of the pentane was removed under a Vigreux column in the presence of a little sodium bicarbonate. An infrared spectrum of the residue indicated that the unreacted chlorobutene had been isomerized to roughly the equilibrium mixture of *cis*- and *trans* isomers (the 12.15 μ band of the *cis* isomer had become very weak, the 12.5 μ band of the *trans* isomer had become strong). Neither the residual pentane nor the adduct interferes with these peaks.

The experiment was repeated with cooling of the flasks to −78°. Hydrogen bromide was passed in for 3 min. Any unreacted hydrogen bromide was destroyed with sodium bicarbonate before letting the mixture warm to room temperature. The infrared spectrum of the mixture after washing, drying and solvent removal again showed isomerization to approximately the equilibrium mixture.

A sample of the *cis*-2-chloro-2-butene was heated at 70° for 24 hr. in the presence of a little pentane, some of the 2-bromo-3-chlorobutane adduct and a little sodium bicarbonate to check for possible isomerization during the processing. The infrared spectrum of the recovered chlorobutane showed that no isomerization had taken place.

Dehalogenation of 2-Bromo-3-chlorobutane with Zinc.—The method used was essentially that of Schubert, Rabinovitch, Larson and Sims.[20] The mixture of 2-bromo-3-chlorobutanes (4.0 mmole) was added all at once to 1.5 g. of zinc dust and 20 cc. of distilled water and the mixture vigorously stirred with a magnetic stirrer. Care was taken to keep the reaction flask at room temperature throughout the reaction. The theoretical volume of gas had been evolved after 1.5 hr. The adduct obtained from the *cis*-chlorobutene gave a 2-butene mixture containing 73% *cis* and 27% *trans*, and the adduct from the *trans*-chlorobutene gave a 2-butene mixture of 74% *cis* and 26% *trans*. The adduct from the Epstein addition to the *cis*-chlorobutene gave a 2-butene mixture containing 71% *cis* and 29% *trans*. The results are considered accurate to ±3%.

Dehydrobromination of 2-Bromo-3-chlorobutane.—The method was similar to that used for the dehydrochlorination of the 2,3-dichlorobutanes described earlier. However, a reaction time of 5–8 hr. was found to be sufficient. After washing and drying as before, the product was usually distilled through a 4-inch Vigreux column before analysis. The average yield of the 2-chloro-2-butene was 70%. The composition of the product mixtures was determined by infrared as described above. The adduct from the *trans*-chlorobutene gave a chlorobutene mixture containing 75% *trans* and 25% *cis*; the adduct from the *cis*-chlorobutene gave a chlorobutene mixture of 71% *trans* and 29% *cis*, and the adduct from the Epstein addition to the *cis*-chlorobutene gave a mixture of 68% *trans* and 32% *cis*.