

was used as a carrier gas at 25 p.s.i. The flow rate was 1.30 ml. per sec. at 225° and 0.86 ml. per sec. at 150°. The elution times are summarized in Table III. The samples of *cis*-stilbene were often contaminated with quinoline and isoquinoline. A commercial mixture of these compounds was used as a solvent in the synthesis²⁰ of *cis*-stilbene. A maximum of 5% of the *trans*-isomer was detected as an impurity in the *cis*-stilbene. It was often considerably less, but there was always some present.

TABLE III
ANALYSIS BY GAS CHROMATOGRAPHY WITH A COLUMN
CONTAINING SILICONE OIL ON CELITE

Compound	Temp., °C.	Elution Time, Min.
<i>cis</i> -Stilbene	225	6.6
<i>trans</i> -Stilbene	225	11.5
Quinoline	225	3.0
Isoquinoline	225	3.5
Diphenylacetylene	226	9.9
Styrene	150	2.6
Styrene dichloride	150	14.3

(20) R. E. Buckles and N. G. Wheeler, *Org. Syntheses*, **33**, 88 (1953).

X-ray powder diagrams. These measurements were carried out by Dr. Norman C. Baenziger of this laboratory. A Straumanis-type camera of 114 mm. diameter was used. The powdered sample was placed in a 0.5-mm. capillary and irradiated with either the copper K α or the iron K α radiation.

Spectra. Infrared spectra were measured in the sodium chloride region with a Perkin-Elmer, Model 21, Spectrophotometer.²¹ This type of data was used in the identification and analysis of samples of α, α' -dichlorobibenzyl dissolved in carbon disulfide. The DL-isomer had two characteristic bands at 645 and 675 cm.⁻¹ which were sufficiently different from the absorption of the *meso*-isomer at those frequencies that an estimate of the composition of mixtures could be made.

Ultraviolet absorption spectra were carried out on a Cary Recording Spectrophotometer, Model 11.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

Addition Reactions of Mixtures of Bromine and Chlorine

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Mixtures of bromine and chlorine have been used as sources of bromine chloride for the synthesis of bromochlorides from cyclohexene, styrene, ethylene, *trans*-cinnamic acid, *cis*- and *trans*-stilbene, and diphenylacetylene. With styrene and cinnamic acid the products isolated were those expected from the addition of positive bromine and negative chlorine to the unsymmetrically substituted double bonds. With *cis*- and *trans*-stilbene stereospecific *trans* addition was observed.

In an earlier report¹ the addition to a double bond of the elements of bromine chloride arising from *N*-bromoacetamide and hydrochloric acid was found to give the products expected of polar, stereospecific *trans* additions. In the present investigation mixtures of bromine and chlorine—presumably in equilibrium with bromine chloride—were used as reagents for addition reactions. The results are given in Table I. Bromochlorides predominated as products in most of the experiments although often in disappointing yields. The bromochloride products obtained are those expected of polar, *trans* addition of bromine chloride to the double bonds just as was found in the investigation¹ involving mixtures of *N*-bromoacetamide and hydrochloric acid.

The predominance of bromochlorides as products is consistent with results reported for the addition reactions of mixtures of bromine and chlorine with

compounds containing double bonds² and triple bonds.³ Of the compounds listed in Table I only ethylene⁴ and cinnamic acid⁵ have been previously reported as reacting with mixtures of bromine and chlorine to give the bromochloride products.

The results with styrene and cinnamic acid show the expected polar addition of bromine chloride to unsymmetrically substituted double bonds in that cinnamic acid yielded 2-bromo-3-chloro-3-phenylpropionic acid and styrene yielded 2-bromo-1-chloro-1-phenylethane. Such a mode of addition has been reported in the case of mixtures of bromine

(2) (a) P. B. D. de la Mare and S. Gandauer, *J. Chem. Soc.*, **36**, (1958); (b) A. Michael, *J. prakt. Chem.*, [2] **60**, 448 (1899); (c) P. Walden, *Ber.*, **30**, 2883 (1897).

(3) N. W. Hansen and T. C. James, *J. Chem. Soc.*, 2979 (1928).

(4) M. Simpson, *Bull. soc. chim. France*, [2] **31**, 409 (1879); J. W. James, *J. Chem. Soc.*, **43**, 37 (1883); M. Delepine and L. Ville, *Bull. soc. chim. France*, [4] **27**, 673 (1920).

(5) (a) N. W. Hanson and T. C. James, *J. Chem. Soc.*, 1955 (1928); (b) E. Erlenmeyer, *Ann.*, **289**, 259 (1896).

(1) R. E. Buckles and J. W. Long, *J. Am. Chem. Soc.*, **73**, 998 (1951).

TABLE I
REPRESENTATIVE EXAMPLES OF ADDITION REACTIONS OF MIXTURES OF BROMINE AND CHLORINE

Unsaturated Compound		Solvent	Products		
Name	Mole		Yield, %	M.P.	Identity ^a
Ethylene ^b	—	CH ₂ Cl ₂	39	106–109 ^c	BrCl
Ethylene ^{b,d}	—	CH ₂ Cl ₂	34	104–106 ^c	BrCl
Cyclohexene	0.56 ^e	CHCl ₃	56	84–94 ^f	BrCl
Styrene	1.0	CHCl ₃	67	26–27	BrCl ^g
<i>trans</i> -Stilbene	0.10	CHCl ₃	52	220–221	<i>erythro</i> -BrCl
			14	193–196	<i>meso</i> -di-Cl
<i>cis</i> -Stilbene	0.055	CHCl ₃	68	99–100	<i>threo</i> -BrCl
			5.5	222–223	<i>erythro</i> -BrCl
<i>cis</i> -Stilbene ^h	0.11	CHCl ₃	18	80–81	<i>threo</i> -BrCl
			2	222–223	<i>erythro</i> -BrCl
			5	121–122	<i>trans</i> -Stilbene
Diphenylacetylene	0.11	CH ₂ Cl ₂	20	173–175	<i>trans</i> -BrCl
			1	159–160	<i>tetra</i> -Cl
Diphenylacetylene	0.11	CHCl ₃	12	159–160	<i>tetra</i> -Cl ⁱ
<i>trans</i> -Cinnamic acid ^j	1.0	CHCl ₃	31	187–188	BrCl
<i>trans</i> -Cinnamic acid ^k	0.068	CH ₂ Cl ₂	73	164–167	di-Cl ⁱ

^a The identity of products is represented as BrCl for a bromochloride, di-Cl for a dichloride, and tetra-Cl for a tetrachloride. ^b The halogen mixture used consisted of 80 g. (0.50 mol.) of bromine and 35.5 g. (0.50 mol.) of chlorine. ^c This was the boiling point at 745 mm. ^d The mixture of bromine and chlorine was not illuminated in this experiment. ^e An 80% excess of the bromine-chlorine mixture was used. ^f This is the boiling point at 15–17 mm. The distilled product also had the properties: d_4^{20} 1.497, n_D^{27} 1.5240. These properties are consistent with those reported¹⁵ for *trans*-1-bromo-2-chlorocyclohexane, which was synthesized by methods other than the addition of bromine chloride to cyclohexene. The success of this experiment depended on the distillation of the product from anhydrous potassium carbonate. A number of experiments in which this was not done gave little or no bromochloride product. ^g This product had the physical and chemical properties reported¹ for 2-bromo-1-chloro-1-phenylethane as well as the melting point given in the table. ^h Several experiments like this one were carried out with *cis*-stilbene which was contaminated by quinoline and isoquinoline. The *threo*-bromochloride (m.p. 99–101°) could not be isolated in a satisfactory manner from the reaction mixtures in these cases. ⁱ No reason was apparent for the formation of the chloride rather than the bromochloride as predominant products in this experiment. The experiments were carried out in essentially the same way in all cases. ^j Similar results could be obtained in methylene chloride. ^k Similar results could be obtained in chloroform even with a 13% excess of bromine over chlorine.

and chlorine with cinnamic acid⁵ and with phenylpropionic acid.³ In the case of propylene with bromine chloride in water both isomeric bromochlorides as well as both bromohydrins were reported^{2a} but the results were shown to be consistent with a polar mechanism involving positive bromine and negative chlorine.

No clear-cut case of stereospecific *trans*-addition of bromine chloride from mixtures of bromine and chlorine has been reported previously. In the present investigation such a stereospecific addition was observed. *cis*-Stilbene yielded *threo*- α -bromo- α' -chlorobiphenyl¹ and *trans*-stilbene gave the *erythro* isomer¹ as predominant products as summarized in Table I. Only one product was reported to be obtained from the reaction of maleic anhydride with mixtures of bromine and chlorine, but no comparison was made with additions to fumaric acid or its derivatives.⁶ In other cases where two stereoisomers were possible both were reported^{3,5a} from additions of bromine chloride.

Bromine chloride, concerning which some controversy has developed in the past as to whether its physical properties could be measured⁷ or not,⁸

has been shown⁹ spectrophotometrically to exist in solution in equilibrium with bromine and chlorine. Its presence is not essential to the explanation of the addition of the elements of bromine chloride in the reaction of olefinic compounds with mixtures of bromine and chlorine, however. Either bromine or bromine chloride could act as a source of positive bromine, and chloride ion (or relatively negative chlorine) could be supplied by either bromine chloride or the bromodichloride ion expected¹⁰ from bromide ion and chlorine.

EXPERIMENTAL

cis-Stilbene. It was observed¹¹ by means of gas chromatography that samples of *cis*-stilbene prepared¹² by the decarboxylation of α -phenylcinnamic acid often contained significant amounts of quinoline and isoquinoline, which came from the solvent used in the decarboxylation.

(8) M. Berthelot, *Compt. rend.*, **94**, 1619 (1882); P. Lebeau, *Compt. rend.*, **143**, 589 (1906); B. J. Karsten, *Z. anorg. Chem.*, **53**, 365 (1907).

(9) See A. I. Popov and J. J. Mannion, *J. Am. Chem. Soc.*, **74**, 222 (1952) and the references cited there.

(10) A. I. Popov and R. E. Buckles, *Inorg. Syntheses*, **5**, 167 (1957).

(11) R. E. Buckles and D. F. Knaack, *J. Org. Chem.*, **25**, 20 (1960).

(12) R. E. Buckles and N. G. Wheeler, *Org. Syntheses*, **33**, 88 (1953).

(6) P. Walden, *Ber.*, **30**, 2883 (1897).

(7) L. W. Andrews and H. A. Carlton, *J. Am. Chem. Soc.*, **29**, 688 (1907); H. Lux, *Ber.*, **63**, 1156 (1930).

Such impure samples of *cis*-stilbene were dissolved in hexane (20 g. in 200 ml.) and washed with four 50 ml. portions of 10% hydrochloric acid. The solution was then washed with 50 ml. of 10% sodium carbonate, and finally with 50 ml. of water. The resulting solution was dried over anhydrous sodium sulfate, cooled to 0°, and filtered to remove the drying agent and most of the *trans*-stilbene present as a contaminant. Fractional distillation yielded *cis*-stilbene, b.p. 135–136° (10 mm.), which appeared to be relatively pure on the basis of the ultraviolet absorption spectrum¹³ and gas chromatography.

A modification of the synthetic procedure¹² for *cis*-stilbene was also carried out. A mixture of 46.0 g. (0.205 mol.) of α -phenylcinamic acid, 280 ml. of quinoline, and 4 g. of copper chromite was heated at 210–220° for 1.25 hr. The mixture was then filtered and distilled at 10 mm. as quickly as possible. The fraction distilling around 104° was recovered quinoline. The crude product, b.p. 125–140° was dissolved in 200 ml. of hexane and then washed and purified as described above. A yield of 21 g. (59%) of *cis*-stilbene, b.p. 135–136° (10 mm.), was obtained.

Other materials. The compounds used in the reactions with bromine chloride were either commercially available or were synthesized by methods given in the Organic Syntheses series. Cyclohexene was purified by fractional distillation, b.p. 81.0–81.5° (739 mm.). Chloroform, and methylene chloride were reagent grade. They were used without further purification.

Addition reactions of bromine-chloride. The addition reactions were carried out in a 1 l., three necked flask fitted by means of spherical joints with: (1) a combination dropping funnel, and gas delivery tube extending close to the bottom of the flask, (2) a stirrer, and (3) a cold-finger condenser which was kept filled during the runs with Dry Ice in a mixture of chloroform and carbon tetrachloride. The reaction flask was kept in an ice-water bath. In each run the desired amount of chlorine was liquefied in a trap cooled in a Dry

(13) R. E. Buckles, *J. Am. Chem. Soc.*, **77**, 1040 (1955).

Ice bath and then weighed. The liquid chlorine was then allowed to distill slowly from the trap by way of the delivery tube into the reaction flask containing the solvent (500 ml. per 35.5 g. of chlorine). An amount of liquid bromine equivalent to the amount of chlorine was then added by way of the dropping funnel and washed in with additional solvent. The bromine-chlorine mixture was illuminated with an ultraviolet lamp because the equilibrium between bromine, chlorine, and bromine chloride is set up more rapidly under these conditions.¹⁴ Actually on the basis of the results with ethylene in Table I this illumination may not be strictly necessary. In the dark an equivalent amount of the unsaturated compound was added in solution or as a gas in the case of ethylene. The reaction mixture was allowed to stand in the dark overnight. The solvent was distilled at 30 to 40 mm. pressure. The residue was then crystallized from a suitable solvent or distilled. For most crystallizations ethanol, carbon tetrachloride, or hexane was used. The results of the experiments are summarized in Table I. The identity of most of the bromochlorides was established by comparison with samples obtained in the earlier investigation¹ by the addition of the elements of bromine chloride from *N*-bromoacetamide and hydrochloric acid. The properties of the bromochloride of cyclohexene compared satisfactorily with those reported¹⁵ for *trans*-1-bromo-2-chlorocyclohexane. The bromochloride of diphenylacetylene checked with the α -bromo- α' -chlorostilbene, m.p. 173–174°, reported by Sudborough.¹⁶ The chloride products listed in Table I were identified by comparison with samples obtained in another investigation.¹¹

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(14) H. G. Vesper and G. K. Rollefson, *J. Am. Chem. Soc.*, **56**, 620 (1934).

(15) M. Mousseron, R. Granger, and J. Valette, *Bull. soc. chim. France*, 244 (1946); M. Mousseron, F. Winternitz, and R. Jacquier, *Bull. soc. chim. France*, 81 (1947).

(16) J. J. Sudborough, *J. Chem. Soc.*, 71, 218 (1897).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Preparation of Homobenzyl and Homoallyl Alcohols by the Hydroboration Method^{1,2}

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H. C. Brown's elegant hydroboration-oxidation method for hydrating olefins provides a convenient route to homoallyl and homobenzyl alcohols. Δ^3 -Cyclopentenol may be prepared from cyclopentadiene, while the pure diastereomeric *threo*- and *erythro*-3-*p*-anisyl-2-butanols arise in good yield from the *cis*- and *trans*-2-*p*-anisyl-2-butenes, respectively. The stereochemistry of the overall hydration is clearly *cis*.

The elegant method of H. C. Brown and his co-workers^{3,4} for accomplishing the hydration of olefins by successive hydroboration and oxidation appeared to offer a convenient route to certain homo-

benzyl⁵ and homoallyl⁶ alcohols of interest in various studies in these laboratories. The alcohols desired were Δ^3 -cyclopentenol (II) and the diastereomeric *threo*- and *erythro*-3-*p*-anisyl-2-butanols (XII and XIII). Therefore, hydration by means of hy-

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(3) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **81**, 247 (1959).

(4) H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1136 (1957).

(5) *e.g.*, (a) S. Winstein, M. Brown, K. C. Schreiber, and A. H. Schlesinger, *J. Am. Chem. Soc.*, **74**, 1140 (1952); (b) S. Winstein and G. C. Robinson, *J. Am. Chem. Soc.*, **80**, 169 (1958).

(6) *e.g.*, (a) S. Winstein, H. M. Walborsky, and K. Schreiber, *J. Am. Chem. Soc.*, **72**, 5795 (1950); (b) S. Winstein, M. Shatavsky, and R. B. Woodward, *J. Am. Chem. Soc.*, **77**, 4183 (1955); (c) S. Winstein and M. Shatavsky, *J. Am. Chem. Soc.*, **78**, 592 (1956).