Reaction of VII with Glacial Acetic Acid.—A mixture of 0.5 g (1.91 mmoles) of VII and 20 ml of glacial acetic acid was heated at reflux temperature for 48 hr. The light yellow solution was cooled and filtered to give 0.25 g of the butadiene XI, mp 152–154° (64%).

Reaction of VII with Bromine. A. 1:1 Ratio.—A solution of 3.1 g (0.019 mole) of bromine in 30 ml of carbon tetrachloride was added dropwise to 5 g (0.019 mole) of VII in 50 ml of the same solvent. Following the addition the solvent was removed using a rotary evaporator. Nmr analysis of the crude reaction product gave a XII/XIII ratio of 4:1. Several recrystallizations of this residue from hexane gave XII, mp 94–96°.

Anal. Calcd for $C_{18}H_{18}Br_2Si$: C, 51.2; H, 4.28; Br, 38. Found: C, 48.0, 48.0; H, 4.14, 4.15; Br, 43.4, 43.3.

When isolated from solution XII tended to decompose rapidly and analysis was difficult. Repeated attempts to isolate XIII free of significant amounts of XII were unsuccessful.

B. 1:2 Ratio.—A solution 12.4 g (0.076 mole) of bromine in 25 ml of carbon tetrachloride was added dropwise to 10 g (0.038 mole) of VII in 30 ml of the same solvent. Initially the bromine color was discharged rapidly; however, heating was utilized during the addition of the second equivalent of bromine. Subsequent to heating overnight (some precipitate present at this time) the solvent was removed with a rotary evaporator. Recrystallization of the residue from a benzene–hexane mixture gave 16 g (72%) of tetrabromo adduct XIV, mp 173–174° dec.

Anal. Calcd for $C_{18}H_{18}Br_4Si$: C, 37.1; H, 3.10; Br, 55.0; Si, 4.80. Found: C, 37.8, 37.7; H, 3.50, 3.47; Br, 55.2, 55.8; Si, 4.82.

Debromination of a Mixture of XII and XIII.—An excess of methylmagnesium bromide was added rapidly to a suspension of 2.0 g (0.047 mole) of a mixture of XII and XIII (ratio *ca.* 4:1). A yellow-green color developed as the exothermic reaction proceeded. After stirring for 1 hr the reaction mixture was poured into a 50:50 ethanol–water mixture. The ether was removed on a rotary evaporator and the solid VII was isolated by filtration, mp 130–133° (65%).

Debromination of XIV.—Using the procedure described above, debromination of 1.0 g (1.72 mmoles) of XIV gave 0.27 g of VII, mp 129–132° (58%).

Preparation of 1,4-Dibromo-*trans,trans*-1,4-diphenylbutadiene (XV).—A mixture of 16 g (0.0275 mole) of the tetrabromosilacyclopentane XIV and 150 ml of ethanol was refluxed for 30 min. Cooling and filtration gave 9.0 g (90%) of XV, mp 121–123°.

Anal. Calcd for $C_{16}H_{12}Br_2$: C, 52.80; H, 3.30; mol wt, 362. Found: C, 52.86, 52.70; H, 3.31, 3.20; mol wt, 362 (by mass spectroscopy).

Reaction of XV with Zinc.—A mixture of 0.5 g (1.36 mmoles) of XV, 0.5 g of zinc dust, and 30 ml of ethanol was refluxed for 18 hr. Filtration, cooling, and concentration gave 0.19 g (68%) of 1,4-diphenyl-*trans,trans*-butadiene (XI), mp 151–154°.

Preparation of 1,4-Dilithio-1,4-diphenylbutadiene (XIX).—To a suspension of 0.5 g (1.36 mmoles) of XV and 20 ml of ether (cooled to ice-bath temperature) was added 2.72 mmoles of *n*-butyllithium. The mixture was allowed to come to room temperature during a 30-min period and then hydrolyzed with 5% hydrochloric acid. Following the usual work-up the residue was recrystallized from cold ethanol to give 0.18 g of XI, mp 151–154° (64.5%).

Reaction of XIX with Dichlorodimethylsilane.—To a solution of XIX, prepared as described above, was added 0.3 g (1.36 mmoles) of dichlorodimethylsilane in 10 ml of THF. After stirring for 1 hr the mixture was hyrolyzed with 5% hydrochloric acid, extracted with ether, and dried, and the solvents were removed. The residue was recrystallized from ethanol to give 0.21 g (58%) of VII, mp 130–133°.

Reaction of XIX with Dimethyltin Dichloride.—A solution of XIX, prepared as described above from 1 g (2.72 mmoles) of XV and 5.74 mmoles of *n*-butyllithium, was added to 0.6 g (2.72 mmoles) of dimethyltin dichloride in 10 ml of ether. After stirring for 1 hr the ether was removed using a rotary evaporator. The residue was extracted with methylene chloride and filtered. Ethanol was added to the filtrate and concentration gave 0.37 g (38.5%) of 1,1-dimethyl-2,5-diphenylstannole (XIX), mp 119–121°. Recrystallization from ethanol gave an analytical sample, mp 120–121°.

Anal. Calcd for $C_{18}H_{18}Sn$: Sn, 33.6. Found:[19] Sn, 33.7, 33.8.

(19) The authors wish to thank Dr. W. J. Considine for part of this analysis.

The Kinetics of the Addition of Bromine to *cis*- and *trans*-Stilbene

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The addition of bromine to *cis*- and *trans*-stilbene in 1,2-dichloroethane, chlorobenzene, and carbon tetrachloride was found to be first order in stilbene and second order in bromine. The results in valeronitrile were too erratic for the order to be established. With tetrabutylammonium tribromide as the sole source of bromine, the reaction in 1,2-dichloroethane, chlorobenzene, and valeronitrile was first order in each reagent. With both bromine and the tribromide present in 1,2-dichloroethane and chlorobenzene the third-order kinetics characteristic of the reaction with bromine were observed. The rate constants increased with increasing concentration of tribromide, but not in a linear fashion. The catalytic effect was found to be decreased at relatively high concentrations of tribromide. In all cases the reaction of *cis*-stilbene was faster than the corresponding reaction of the *trans* isomer. The rates of bromine addition tended to be higher in the more polar solvents. These kinetic results are consistent with polar mechanisms involving an electrophilic attack by bromine. The complex resulting from this interaction can apparently give dibromide product in a variety of ways.

Data on the mechanism of addition of bromine and other halogens to carbon–carbon double bonds have been reported[1-3] for a number of systems. In most

cases[2,4] the reactions have involved an electrophilic attack, but, in some cases[2,3,5,6] involving double bonds substituted with electron-withdrawing groups, a nucleophilic attack is also of importance.

(1) S. V. Anantakrishnan and R. Venkataraman, *Chem. Rev.*, **33**, 27 (1943).
(2) P. B. D. de la Mare, *Quart. Rev.* (London), **3**, 126 (1949).
(3) P. W. Robertson, *Rev. Pure Appl. Chem.*, **7**, 155 (1957).

(4) J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 214.
(5) R. E. Buckles and J. P. Yuk, *J. Am. Chem. Soc.*, **75**, 5048 (1953).
(6) R. E. Buckles and L. Harris, *ibid.*, **79**, 886 (1957).

Of particular interest for considering these mechanisms is the case of stilbene. Kinetic data on the addition of bromine to the *trans* isomer have been reported for solutions in carbon tetrachloride,[7] bromobenzene,[8] acetic acid,[7,9,10] methanol,[11,12] and water,[13] while kinetic data on the addition of bromine to the *cis* isomer have involved only methanol[12] and water[12] as solvents. Quantitative investigations[14,15] showed that the stereospecificity of the *trans* addition of bromine to *cis*-stilbene decreased with increasing polarity of solvent. It was further found[14] that the stereospecificity was restored in the presence of a quaternary ammonium tribromide, dibromobromate (I), salt.

In the present investigation the kinetics of the addition reactions of bromine and tetrabutylammonium tribromide with *cis*- and *trans*-stilbene have been studied in carbon tetrachloride, chlorobenzene, 1,2-dichloroethane, and valeronitrile as solvents.

The rate constants for the addition of bromine to *cis*- and *trans*-stilbene in the four solvents are summarized in Table I. In carbon tetrachloride, chlorobenzene, and 1,2-dichloroethane the data were best fit by the rate law of eq 1 where [E] represents the con-

$$-d[Br_2]/dt = k[Br_2]^2[E] \tag{1}$$

centration of the stilbene. Although considerable variation in individual values of k was sometimes observed no significant trends in these values were observed with systematic changes in the concentration of either reagent. In valeronitrile no such clean-cut results were obtained. Relatively rapid initial con-

sumption of bromine was followed by extensive inhibition of the reaction. It was shown by experiments with the *meso* dibromide that the addition was not appreciably reversible at 25°. Since solutions of bromine in valeronitrile in the absence of stilbene showed no such rapid uptake of bromine it seems unlikely that an impurity which was highly reactive to bromine could account for the results. For the present it will be assumed that the initial reaction rates give the order of magnitude of the rate constants for the addition of bromine in this solvent, but whether the reactions were second or third order could not be determined.

Kinetic studies on the reaction of tetrabutylammonium tribromide with *cis*- and *trans*-stilbene were carried out in chlorobenzene, 1,2-dichloroethane, and valeronitrile. The tribromide salt was insoluble in carbon tetrachloride. The results are summarized in Table II. In these cases the results best fit the rate law of eq 2. No significant trends in the values of the

$$-d[R_4NBr_3]/dt = k'[E][R_4NBr_3] \tag{2}$$

rate constant with systematic changes in the concentration of either reagent were observed. Again the least precise results were obtained in valeronitrile, with a varying tendency toward inhibition being observed. The presence of tetrabutylammonium bromide showed no marked catalytic effect such as was observed[6] with crotonic acid. The slight upward trend in k' observed with *trans*-stilbene in 1,2-dichloroethane as the concentration of the bromide was increased was probably caused by the more favorable environment for the polar addition mechanism.

TABLE I
Third-Order Rate Constants for the Reaction of Bromine with *cis*- and *trans*-Stilbene at 25°

Isomer	Solvent	D^a	Concn range, $M \times 10^3$	Titration method[b]	No. of runs	$k,^c$ l.^{2} mole^{-2} sec^{-1}
trans	CCl$_4$	2.2	5–12	A	10	0.032 ± 0.006
cis	CCl$_4$		5–10	A	3	0.102 ± 0.015
trans	PhCl	5.7	2–11	A	5	3.9 ± 0.6
cis	PhCl		2–10	A	4	10.0 ± 0.5
trans	(CH$_2$Cl)$_2$	10.2	2–12	A	9	58.4 ± 2.4
trans	(CH$_2$Cl)$_2$		0.5–10	P	26	59.6 ± 5.8
cis	(CH$_2$Cl)$_2$		3–6	A	7	244 ± 8
cis	(CH$_2$Cl)$_2$		0.5–7	P	8	258 ± 31
trans	BuCN[d]	17.4	7–14	A	3	74 ± 68[e]
cis	BuCN[d]		4–11	A	3	195 ± 164[f]

[a] Values of the dielectric constant (D) are for around room temperature (20–25°). They are taken from A. A. Maryott and E. R. Smith, "Table of Dielectric Constants of Pure Liquids," National Bureau of Standards Circular 514, Washington, D. C., 1951. [b] Iodometric methods of analysis were used. A represents the amperometric method and P stands for the potentiometric method. [c] The precision sets the 95% confidence limits of the average value. [d] Initial rates were estimated in valeronitrile because of the inhibition observed as the reaction progressed. [e] The initial second-order rate constant was 0.67 ± 0.25 l. mole^{-1} sec^{-1}. [f] The initial second-order rate constant was 1.4 ± 1.4 l. mole^{-1} sec^{-1}.

TABLE II
Second-Order Rate Constants for the Reaction of Tetrabutylammonium Tribromide with *cis*- and *trans*-Stilbene at 25°

Isomer	Solvent	Concn range, $M \times 10^3$	No. of runs	$10^4k',^a$ l. mole^{-1} sec^{-1}
trans	PhCl	5–15	5	0.20 ± 0.05
cis	PhCl	5–15	2	2.3 ± 1.4
trans[b]	(CH$_2$Cl)$_2$	9–11	5	3.2 ± 0.5[c]
cis	(CH$_2$Cl)$_2$	6–15	3	7.9 ± 0.3[c]
trans	BuCN	7–13	3	1.2 ± 1.1
cis	BuCN	8–17	3	2.0 ± 0.9

[a] The precision sets the 95% confidence limits of the average value. [b] Tetrabutylammonium bromide was present in the reaction mixtures in concentrations varying from 0 to 3 × 10^{-2} M. A slight increase in $k'(2.7 \times 10^{-4}$ to 3.5 × 10^{-4}) was observed as the concentration of the bromide salt was increased. The average value given is that obtained by extrapolation to 0 concentration of bromide. [c] Values of this order of magnitude were also obtained using potentiometric titrations.

Experiments with both bromine and tetrabutylammonium tribromide present were carried out with *cis*- and *trans*-stilbene in 1,2-dichloroethane and chlorobenzene. An unexpected increase in the values of the third-order rate constant (k) was observed, but no simple dependence on the concentration of tribromide was apparent. A typical series of experiments for *cis*-stilbene in 1,2-dichloroethane is summarized in Table III. Similar results in which the accelerating effect of tribromide either fell off or decreased with increasing tribromide concentration were observed with the *trans* isomer and in chlorobenzene as a solvent. Maximum values of k as great as seven times the values

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(9) I. Ting and P. W. Robertson, *J. Chem. Soc.*, 628 (1947).

(10) H. Sinn, *Angew. Chem.*, **69**, 754 (1957).

(11) P. D. Bartlett and D. S. Tarbell, *J. Am. Chem. Soc.*, **58**, 466 (1936).

(12) J. E. Dubois and G. Barbier, *Tetrahedron Letters*, 1217 (1965).

(13) J. R. Atkinson and R. P. Bell, *J. Chem. Soc.*, 3260 (1963).

(14) R. E. Buckles, J. M. Bader, and R. J. Thurmaier, *J. Org. Chem.*, **27**, 4523 (1962).

(15) G. Heublein, *J. Prakt. Chem.*, **31**, 84 (1966).

Table III

Third-Order Rate Constants for the Reaction of Bromine with cis-Stilbene in the Presence of Tetrabutylammonium Tribromide in 1,2-Dichloroethane at 25°
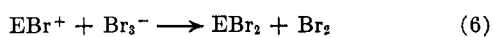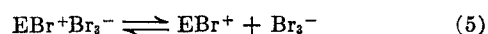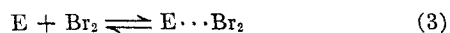
[Bu$_4$NBr$_3$] × 10^3, M	[Br$_2$] × 10^3, M	[E] × 10^3, M	k × 10^{-2}, l.^{2} mole^{-2} sec^{-1}
1.42	8.30	7.12	3.0
2.85	8.30	7.12	3.7
4.00	4.81	3.56	4.0
4.27	8.30	7.12	4.2
5.69	8.30	7.12	5.3
7.12	8.30	7.12	7.3
8.00	4.81	3.56	5.3
8.54	8.30	7.12	14.6
9.96	8.30	7.12	17.0
11.4	8.30	7.12	14.3
12.0	4.81	3.56	11.0

without tribromide present were observed for *trans*-stilbene in chlorobenzene. For the other combinations the results were similar but the effects were smaller.

As would be expected the less stable *cis*-stilbene reacted consistently faster than the more stable *trans* isomer. This type of observation has been reported[12] for reactions in water and methanol but these cases are not strictly comparable with the present examples since bromide ion was present, and no corrections were made for the concentrations of tribromide ion and bromine in the reaction media.

The visual end point used[6] for the iodometric determination of bromine in solvents mixed with aqueous methanol was not suitable for the concentration range (10^{-4}–10^{-2} M) used in the present work. Instead two electrometric methods were used. For most of the experiments an amperometric titration with a dead-stop end point was used. For a considerable number of experiments in 1,2-dichloroethane (Tables I and II), however, a potentiometric titration was used. This potentiometric method was considerably less precise, presumably because of difficulties with the mixing of solutions in the electrode chamber.

The kinetic results for the addition of bromine to *cis*- or *trans*-stilbene are consistent with a polar mechanism such as that outlined in eq 3–6. The initial elec-

$$E + Br_2 \rightleftharpoons E \cdots Br_2 \tag{3}$$

$$E \cdots Br_2 + Br_2 \rightleftharpoons EBr^+Br_3^- \tag{4}$$

$$EBr^+Br_3^- \rightleftharpoons EBr^+ + Br_3^- \tag{5}$$

$$EBr^+ + Br_3^- \longrightarrow EBr_2 + Br_2 \tag{6}$$

trophilic attack to give the charge-transfer-complex $E \cdots Br_2$ (eq 3) would be expected to be an unfavorable equilibrium which is rapidly set up. The ionization to give the ion pair $EBr^+Br_3^-$ (eq 4) could be relatively slow, in which case the rate law would be given by eq 7 where k refers to a rate constant, K refers to an equilibrium constant, and the subscript identifies the reaction step. Such a rate law is consistent with that

$$-d[Br_2]/dt = K_3k_4[E][Br_2]^2 \tag{7}$$

observed experimentally (eq 1). Although less likely, the dissociation of the ion pair to solvated ions (eq 5) could be slow. Much more likely would be a slow nucleophilic attack of tribromide ion on the cation EBr^+ to give the product EBr_2 (eq 6). In either of these cases rate laws consistent with that of eq 1 would

be derived. A similar rate law would be obtained if a nucleophilic attack such as that shown in eq 8 were slow or if $EBr^+Br_3^-$ rearranged—possibly by way of the equilibrium of eq 5—to give a new ion pair with the tribromide ion in a suitable position so that it would react directly with EBr^+ to give the dibromide.

$$E \cdots Br_2 + Br_2 \longrightarrow EBr_2 + Br_2 \tag{8}$$

Stereospecific *trans* addition would be expected for all of these mechanisms if the nucleophilic attack were on the side opposite to the bromine atom of the symmetrical bromonium ion **1**. This species would be expected[14,15] to be favored in relatively nonpolar solvents such as carbon tetrachloride. In order to account for the loss of stereospecificity during the addition of bromine to *cis*-stilbene in more polar solvents such as the others listed in Table I, unsymmetrical bromonium ion **2**[14] and 2-bromo-1,2-diphenylethyl cation **3**,[15] which can rotate about the central C–C bond before the nucleophilic attack, have been suggested. A species such as **2** has also been suggested to account for the effect of substituents on the rate of addition of bromine to styrenes.[16]
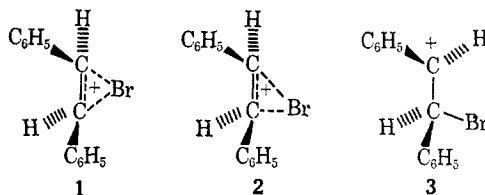
The trend to higher rates of reaction in the more polar solvents as shown in Table I is consistent with the polar mechanism of addition involving ionization and possible ion-pair dissociation as outlined in eq 3–6. This same sort of trend is apparent in Table IV which summarizes rate constants for the addition of bromine to *trans*-stilbene which have been reported in the literature. Table IV also shows the trend to a rate law first order in both stilbene and bromine in the more polar solvents—especially those with hydroxyl groups capable of aiding ionization and dissociation of $E \cdots Br_2$ without the help of a second bromine molecule.

Table IV

Rate Constants for the Addition of Bromine to *trans*-Stilbene in Various Solvents

Solvent	D^a	Temp, °C	Order in Br$_2$	k^b	Ref
CCl$_4$	2.2	35	2	0.20	7
C$_6$H$_5$Br	5.4	20	2	2.55	8
HOAc	6.2	35	2	185	7
HOAc		24	2	37^c	9
HOAc		24	1	0.30	9
HOAc		68.5	1	0.6^d	10
MeOH	32.6	0	1	3.33	11
H$_2$O	78.5	25	1	7.8 × 10^5	13

^{a} Values of the dielectric constants are from the same source as listed in Table I. ^{b} Rate constants are either in l.^{2} mole^{-2} sec^{-1} or in l. mole^{-1} sec^{-1} depending on the order with respect to bromine. ^{c} This value is one-fourth of that given in ref 9, but it is the one which is consistent with the data given. ^{d} This value was estimated from the figure in ref 10.

The second-order rate law (eq 2) observed for the reaction of *cis*- and *trans*-stilbene with tetrabutylam-

(16) K. Yates and W. V. Write, *Tetrahedron Letters*, 1927 (1965).

monium tribromide is also consistent with a polar mechanism of bromine addition. The dissociation of eq 9 must be considered since the tribromide would be expected to be a very poor electrophile. Following

$$R_4N^+Br_3^- \rightleftharpoons R_4N^+Br^- + Br_2 \qquad (9)$$
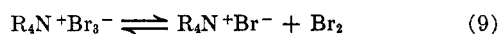
the electrophilic attack of eq 3, an ionization such as eq 10 and a final slow step such as eq 11 would complete the addition. This mechanism would lead to the rate

$$E\cdots Br_2 \rightleftharpoons EBr^+Br^- \qquad (10)$$

$$EBr^+Br^- + R_4N^+Br^- \longrightarrow EBr_2 + R_4N^+Br^- \qquad (11)$$
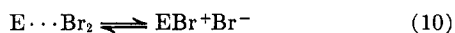
law of eq 12 which is consistent with the experimental rate law given in eq 2. The ionization of eq 10 might

$$-d[R_4NBr_3]/dt = K_3K_9K_{10}k_{11}[E][R_4NBr_3] \qquad (12)$$

not be necessary since the bromide could attack $E\cdots Br_2$ in a slow step which would lead to a third-order rate law also consistent with eq 2. Neither steps 3 and 10, nor the dissociation of EBr^+Br^- could be slow, since in such a situation the addition of bromide salt would be expected to suppress the rate by favoring the reversal of step 9. Also steps 4–6 could not be involved since they and similar steps would require that the reaction be second order with respect to tribromide.

The rate enhancement observed when *cis*- or *trans*-stilbene reacted with bromine in the presence of tetrabutylammonium tribromide could be explained in terms of the steps 3 and 4 followed by a slow step (13).

$$EBr^+Br_3^- + R_4N^+Br_3^- \longrightarrow EBr_2 + Br_2 + R_4N^+Br_3^- \qquad (13)$$
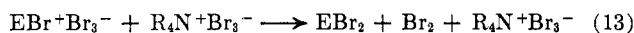
In this slow step the tetrabutylammonium tribromide would be expected to come into the ion aggregate with the tribromide ion *trans* to the bridging bromine atom. This approach would lead to an effective completion of the stereospecific *trans* addition. At the same time the formation of an ion aggregate as shown in the equilibrium of eq 14 with the tribromide ion in some position less effective than *trans* to the bridging bromine could lead to the catalytic effect falling off as the tribromide concentration was increased. This situation would lead to the rate law of eq 15. In fact the involvement of still higher ion aggregates containing two molecules of tribromide salt but not reacting to give the product would lead to a rate law similar to eq 15, but

$$EBr^+Br_3^- + R_4N^+Br_3^- \rightleftharpoons EBr^+R_4N^+(Br_3^-)_2 \qquad (14)$$
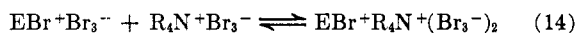
$$-d[Br_2]/dt = \frac{k_3k_4k_{13}[E][Br_2][R_4NBr_3]^2}{k_{-3}k_{-4}(k_{-3}k_{-4}k_{14} + k_{-3}k_{13})[R_4NBr_3]} \qquad (15)$$

with a $[R_4NBr_3]^2$ term in the denominator. Such a rate law would have a maximum value for the apparent rate constant at some concentration of tribromide. It seems unlikely that the observed falling off of the catalytic activity of the tribromide salt could be explained by a shift to a different slow step such as eq 4 or 6 on which external tribromide would have no direct kinetic effect. Such a shift would not be expected with increasing concentration of the tribromide salt.

The restoration of stereospecific *trans* addition of bromine in the presence of tribromide ion in the more polar solvents, which was reported[14] earlier, was confirmed in the present work. This stereospecificity is consistent with product-forming steps such as eq 11 or 13. In these cases EBr^+ (probably structure **2** rather than **3**) must react faster at the side opposite to the

bromine atom to form the product and, thus, have less time to isomerize than it would in the cases where no tribromide or bromide salts were present and the ion pair would have to dissociate (eq 5) or rearrange before the nucleophilic attack to form product could be completed.

Experimental Section

Reagents.—The reported preparation[17] of *cis*-stilbene was modified as previously reported.[18] Some preparations were further purified by chromatographic adsorption on activated alumina (Merck) followed by elution with hexane. Other preparations were crystallized at Dry Ice temperatures. In either case the final product was redistilled, bp 92.5–93.0° (5 mm). In neither case could any *trans*-stilbene or quinoline be detected in the product by gas chromatography[18] or by ultraviolet absorption spectra.[14,19]

Commercial preparations of *trans*-stilbene were crystallized from hexane to give a product of mp 124.5–125.5°.

Tetrabutylammonium bromide was synthesized by the reaction of tributylamine with butyl bromide in either butyl acetate or ethyl acetate as described[6] earlier. Yields of purified product between 30 and 40% were obtained. As before[6] on the basis of the analyses for carbon in several samples the product (melting point in a sealed tube 116.5–117.5°) did not seem to be contaminated with more than 1% tetrabutylammonium acetate.

Tetrabutylammonium tribromide, mp 73–74° (from acetic acid–carbon tetrachloride), was prepared as reported[6,20] earlier.

Bromine was purified by the procedure of Bauer and Daniels[21] except that the crystallization step was omitted.

Solvents.—Fisher Spectranalyzed reagent grade carbon tetrachloride was used without further purification. Technical grade chlorobenzene was purified with concentrated sulfuric acid as described[22] in the literature. Samples of bp 131.9–132.0° (745 mm) were used. 1,2-Dichloroethane was purified with concentrated sulfuric acid as described[23] earlier. Attempts to shorten the purification procedure or to use activated alumina for the purification yielded solvent which was somewhat reactive to bromine. Valeronitrile, bp 140.5–141.0° (745 mm), was obtained by the purification procedure of Jeffery and Vogel.[24] Gas chromatographic analyses of the solvents showed only the single peaks characteristic of the solvent except for the case of valeronitrile. This solvent showed a second peak with about half the retention time of the solvent peak. The impurity peak represented about 0.7 mole %.

Methods of Analysis.—The amperometric method[25] of iodometric analysis with a dead-stop end point was the most satisfactory one used. A Sargent Model P amperometric titrator was used with a Leeds–Northrup Model 2420A galvanometer in place of the ammeter. The applied emf across the two platinum electrodes was 0.035 v. The sample containing bromine, a tribromide salt, or both was mixed with excess 2% methanolic potassium iodide. Standardized aqueous thiosulfate was added as the solution was stirred until only a faint yellow color was visible. Further careful addition of the titrant led to a point of minimum current which was taken as the end point. The end point was sharply defined with just 1 drop of the thiosulfate solution usually used (*ca.* 5×10^{-3} *M*). Equilibration between the electrodes seemed to be virtually instantaneous.

The potentiometric method of analysis used a Fisher automatic titrimeter fitted with a platinum electrode in a mixing chamber and a calomel reference electrode. The aqueous thiosulfate used as a titrant was delivered directly into the mixing chamber so that the platinum electrode responded rapidly and the end point

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was not passed during the titration. Slower mixing between the mixing chamber and the bulk of the solution took place through several holes in the walls of the chamber. Only solutions in 1,2-dichloroethane were analyzed by this method. Samples were mixed with excess 1% methanolic potassium iodide and then titrated with standardized aqueous thiosulfate ($ca.$ 5×10^{-3} M) to a potential of -0.166 ± 0.004 v.

A third method of analysis, which was investigated, involved a spectrophotometric determination of triiodide ion. Standardized solutions of iodine in the presence of excess potassium iodide were made up in the mixed solvent, 10 vol. % 1,2-dichloroethane in 95% ethanol. Spectra of these solutions led to the determination of the molar absorbtivity of triiodide ion of $(27.2 \pm 1.9) \times 10^3$ mole cm^{-1} l.$^{-1}$ at 352 mμ. This method of analysis was applied to the addition of bromine to $trans$-stilbene in 1,2-dichloroethane by the dilution of measured samples with three volumes of 1% potassium iodide in 95% ethanol and the determination of the absorbance at 352 mμ. The method gave rise to erratic values of rate constants which were consistent only as to order of magnitude with those obtained by the other two methods of analysis (Table I).

With all methods of analysis it was shown that the presence of either dibromide ($meso$- or dl-α,α'-dibromobibenzyl) did not affect the analytical procedure appreciably if the quenched solution were allowed to stand no longer than 30 min.

Kinetic Experiments.—All kinetic experiments were carried out in a dark room with a photographic safelight used for illumination during any manipulations. Stock solutions of reagents and pure solvent were brought to temperature equilibrium in a constant-temperature bath at $25.00 \pm 0.03°$. Reaction mixtures were prepared by mixing measured volumes of stock solutions and of pure solvent in the reaction flask immersed in the constant-temperature bath. The solution of the brominating agent (bromine, tetrabutylammonium tribromide, or a mixture of the two) was added last as the reaction flask was swirled. For mixtures undergoing fast reactions the point of time for the addition of half of the volume of brominating agent was taken as the beginning of the reaction. It was determined that with the concentrations of stock solutions used (up to 0.1 M) no significant change in total volume took place during mixing.

Measured volumes were withdrawn from the reaction mixtures and mixed with excess methanolic potassium iodide. For rapid reactions the point of time for the discharge of half of the volume of sample into the potassium iodide solution was taken as the time of quenching. Iodometric analyses were conducted as described above.

For very rapid reactions with cis-stilbene a self-leveling sample device was mounted above the reaction flask. A sample was quickly forced into the self-leveling pipet by nitrogen pressure and then discharged by means of gravity into the quenching solution. It was possible to withdraw samples reproducibly within 120 sec of the start of the reaction with this device. Standardization with water showed that the pipet delivered 10.86 ± 0.03 ml at $25.00 \pm 0.03°$.

A number of experiments were run concurrently with matched control experiments to test the effect of added factors on the extent of reaction of bromine with $trans$-stilbene in 1,2-dichloroethane. No significant effect was observed with glass beads present, with $meso$-dibromide present so that it precipitated during the reaction, with the solvent saturated with water, or with the solvent saturated with oxygen. Significantly faster reactions were observed when the reactions were carried out in diffuse daylight, however.

Solutions of the $meso$ dibromide in valeronitrile either with or without bromine present were allowed to stand at 25°. No evidence of elimination of bromine from the dibromide was observed.

Treatment of Kinetic Data.—Integrated forms of eq 1 and 2 were used graphically and by least-squares fitting of the best straight line in order to obtain the most significant value of the rate constant from each set of data. In experiments with both bromine and tetrabutylammonium tribromide present the concentration of bromine was treated as variable and that of tribromide as a constant. The integrated forms of eq 1 were used, with the concentration of the tribromide salt being included in the rate constant.

Product-Isolation Experiments.—Small-scale reactions involving 0.27 g (1.8×10^{-3} mole) of stilbene in 45 ml of the solvent were treated with 5 ml of 0.45 M bromine solution in the dark. After time for complete reaction at room temperature had been allowed the solvent was removed in an evaporator. The composition of the residual dibromide product was estimated by means of the infrared spectrum of a mineral oil mull. The ratio of the absorbance of the band at 535 cm^{-1} (characteristic[14] of the dl isomer) to that of the band at 554 cm^{-1} (characteristic[14] of the $meso$ isomer) was used as a measure of the composition. This ratio of absorbance showed fairly significant changes with the composition of mixtures of the dibromides at low percentages of the $meso$ isomer, but very small changes at high percentages of the $meso$ isomer. On the other hand, the inverse ratio of absorbances was useful at high concentrations of the $meso$ isomer. The addition of bromine to cis-stilbene in 1,2-dichloroethane or chlorobenzene was found to give a dl dibromide product contaminated by about 35% of the $meso$ isomer. When 0.9 g (1.9×10^{-3} mole) of the tetrabutylammonium tribromide was added to the reaction mixture either instead of the bromine or along with the bromine the dl dibromide was contaminated with little or no $meso$ isomer.

Registry No.—cis-Stilbene, 645-49-8; $trans$-stilbene, 103-30-0; α,α-dibromo-t-stilbene, 3720-09-0; α,α-dibromo-$meso$-stilbene, 3720-09-0.