Equilibria and UV-Spectral Characteristics of BrCl, $BrCl_2^-$, and Br_2Cl^- Species in 1,2-Dichloroethane − Stereoselectivity and Kinetics of the Electrophilic Addition of these Species to Alkenes

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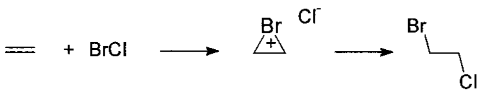
UV/Vis spectrophotometric measurements have been used to determine the equilibrium constants and the absorption spectra of $Bu_4N^+Br_2Cl^-$ and $Bu_4N^+BrCl_2^-$ species in 1,2-dichloroethane (DCE) at 25 °C. The formation constants and the absorption spectra of BrCl from Br_2 and Cl_2 and of $Bu_4N^+Cl_3^-$ species from $Bu_4N^+Cl^-$ and Cl_2 were also determined in this solvent at 25 °C. The kinetics and the products of bromochlorination of several aryl-substituted olefins with BrCl, with Br_2 in the presence of an excess of $Bu_4N^+Cl^-$ (Br_2/Cl^-), and with BrCl in the presence of an excess of $Bu_4N^+Cl^-$ ($BrCl/Cl^-$) were investigated in DCE at different temperatures. The kinetics and product distribution data for the reactions with Br_2/Cl^- or $BrCl/Cl^-$ are interpreted on the basis of a mechanism involving a product- and rate-determining nucleophilic attack by chloride on the olefin-halogen (Br_2 or BrCl) π complex. The data relating to the electrophilic addition of BrCl are interpreted in terms of the initial formation of a 1:1 olefin–BrCl π complex, the ionization of which, catalyzed by a second halogen molecule, gives a bromonium (or β-bromocarbenium) $BrCl_2^-$ ion pair able to collapse to the corresponding bromochloro adducts. A significant proportion of the ion pair intermediates may, however, actually be present as bromonium (or β-bromocarbenium) Br_2Cl^- and Br_3^- ion pairs, and the collapse of these should be responsible for the formation of the dibromides in BrCl addition.

Introduction

Addition of electrophilic halogens to carbon−carbon double bonds is probably the most commonly presented example of a typical reaction of unsaturated systems,[1,2] and organic chemistry textbooks devote considerable space to discussion of this apparently simple reaction. However, while the electrophilic bromination of olefins is a well studied reaction that has recently attracted renewed interest,[3−5] the electrophilic addition of mixed halogens has received much less investigation.[1,2] Among the possible combinations of mixed halogens, only the ClF, ICl, and IBr species are well defined, isolable compounds.[1] Vicinal bromochlorides may, however, be obtained by addition of alkenes to the equilibrium mixture of Br_2, Cl_2, and BrCl;[1] the different reactivities of the three halogens favor the formation of the bromochloride(s) as the main product.[1] Although large variations are found in the product distributions reported by various authors,[6] the regio- and stereochemical behavior of BrCl addition to olefins has been interpreted on the basis of an $AdEC_1$-type mechanism involving the attack of chloride ion onto a bromonium ion intermediate bridged to a greater or lesser extent.

In the light of more recent investigations into Br_2 addition to alkenes, however, it is highly likely that the addition of BrCl is also a much more complicated process than the simple representation in Equation (1) would suggest. At least one charge-transfer complex should precede the ionic intermediate. The formation of a complex between ethylene and BrCl in the gas phase has recently been detected[7] by rotational spectroscopy, and so it is possible that this type of intermediate also occurs in solution. The ionization of this complex should give the ionic intermediate, and the nature of the cationic moiety (bridged, partially bridged, or open) should mainly depend on the olefin structure. In relatively nonpolar aprotic solvents, which are unable to assist ionization by acting as electrophiles to remove Cl^- through hydrogen bonding, it is possible that a second halogen molecule may be involved in the electrophilic step to displace Cl^- as a $BrCl_2^-$ and/or Br_2Cl^- ion. The formation of $BrCl_2^-$ and Br_2Cl^- ions through addition of Br_2 to an aqueous solution of Cl^- ions is a well-known process.[8] The electronic spectra of these species and the equilibrium constants for the reactions reported in Scheme 1 have recently been determined[9] in water, but no data concerning the formation of these anions in low polarity aprotic solvents are available.



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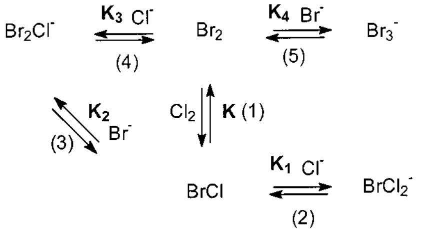


Scheme 1

However, information about the stability of these ionic species in aprotic solvents may be important for more complete comprehension of the mechanism of BrCl addition. The counteranion of the ionic intermediates may indeed determine the nature and stereochemistry of the product. The polyanions can donate Br^- or Cl^- during the nucleophilic step, resulting in the corresponding dibromides or bromochlorides. Furthermore, when partially bridged bromonium or β-bromocarbenium ions are involved, the nature of the anion, affecting the lifetime of the intermediates, determines the product stereochemistry.

Finally, it is noteworthy that both $BrCl_2^-$ and Br_2Cl^- ions are able to add[10−12] to double and triple bonds as electrophilic species to give the corresponding bromochlorides in a stereospecific fashion.

Here we report an investigation of the equilibria involving Br^-, Cl^-, Br_3^-, $BrCl_2^-$, and Br_2Cl^- anions in a solvent − 1,2-dichloroethane − of moderate polarity, and we examine the influence of these equilibria on the product distribution of electrophilic addition of BrCl to double bonds. We also report new kinetic evidence relating to the ability of the $BrCl_2^-$ and Br_2Cl^- species to act as electrophiles.

Results and Discussion

UV/Vis Spectroscopic Data Concerning Reactions between Cl^- and Br_2

The UV/Vis spectra of equimolar solutions (ca. 10^{-3} M) of Br_2 and tetrabutylammonium chloride (TBACl), taken in 1,2-dichloroethane (DCE) at 25 °C, featured a maximum around 258 nm that may be attributed to the formation of $Bu_4N^+Br_2Cl^-$. Identical λ_{max} and band shape were found after dilution of these solutions from 10^{-3} to 2×10^{-5} M. Below this concentration, however, the band shape changed and small bathochromic shift could be detected. At constant $[Br_2]$ (2×10^{-4} M), moreover, an increase in [TBACl] resulted in a hyper- and hypsochromic shift of the absorption band, the maximum of which was around 240 nm at higher TBACl concentrations (ca. 6×10^{-2} M). The observed dependence of the absorption maximum on the reagent concentration was totally inconsistent with the sole presence of equilibrium (4) of Scheme 1, and clearly pointed to the formation of other species absorbing in the same spectral range. The most plausible candidates were $Bu_4N^+BrCl_2^-$ and $Bu_4N^+Br_3^-$, formed through equilibria 3, 2, and 4. The equilibria reported in Scheme 1 had already been investigated in water,[9] and the equilibrium constants K_2 and K_3 and the molar extinction coefficients of Br_2Cl^- species had been determined on the basis of spectral changes of solutions of $BrCl_2^-$ in HCl with variable concentrations of added Br^-. The observed absorbance at each wavelength (1 cm cell) as a function of $[Br^-]$ was fitted to Equation (2) (where ε_1 to ε_6 are the extinction coefficients of BrCl, $BrCl_2^-$, Br_2Cl^-, Br_2, Br_3^-, and Br^-), using known values for K_1 and K_4, and for ε_1, ε_2, ε_4, ε_5, and ε_6.

$$A_\lambda = \left[\frac{\left[BrCl_2^-\right]_T}{\left(1 + \frac{1}{K_1\left[Cl^-\right]} + \frac{K_2\left[Br^-\right]}{K_1\left[Cl^-\right]} + \frac{K_2\left[Br^-\right]}{K_1K_3\left[Cl^-\right]^2} + \frac{K_2K_4\left[Br^-\right]^2}{K_1K_3\left[Cl^-\right]^2}\right)} \right] \left[\varepsilon_2 + \frac{\varepsilon_1}{K_1\left[Cl^-\right]} + \frac{\varepsilon_3K_2\left[Br^-\right]}{K_1\left[Cl^-\right]} + \frac{\varepsilon_4K_2\left[Br^-\right]}{K_1K_3\left[Cl^-\right]^2} + \frac{\varepsilon_5K_2K_4\left[Br^-\right]^2}{K_1K_3\left[Cl^-\right]^2} \right] + \varepsilon_6\left[Br^-\right] \quad (2)$$

The application of this approach to determine the formation constant of Br_2Cl^- species in DCE therefore implied a preliminary determination of K_1 (K_4 is already known[13]) and of the extinction coefficients of BrCl and $BrCl_2^-$ species. Furthermore, since the equilibrium constant for the BrCl species in DCE was unknown, this value (at 25 °C) was determined initially, together with the formation constant of the Cl_3^- anion in this solvent.

Equilibrium Constant for BrCl Formation

The UV/Vis spectra of solutions of Br_2 and Cl_2 in DCE were measured in the 230−500 nm range at 25 °C. An absorption band attributable to BrCl, with $\lambda_{max} = 370$ nm, was apparent in all solutions. In order to determine the molar extinction coefficients (ε) for BrCl species, solutions containing excess amounts of one or other halogen were prepared, to repress dissociation. The wavelengths at which the halogen in excess displayed its minimum, 320−330 nm for Br_2 and 440−460 for Cl_2, were chosen to determine the extinction coefficients of BrCl. Assuming complete suppression of dissociation, the measured absorbances were the sum of the absorbances of BrCl and the excess halogen

$$A_\lambda = \varepsilon_{BrCl} \times l \times c_{BrCl} + \varepsilon_{hal}\, l \times c_{hal} \quad (3)$$

where:

ε_{BrCl} and ε_{hal} are the extinction coefficients of BrCl and the excess halogen, respectively,

l is the optical path length,

c_{BrCl} and c_{hal} are the concentrations of BrCl and excess halogen, respectively.

From Equation (3), the ε values for BrCl were calculated using the known extinction coefficients of the excess halogen.

The concentrations of Cl_2, Br_2, and BrCl present in equimolar mixtures of Br_2 and Cl_2 could also be calculated by the method given in a previous paper,[14] on the basis of absorbance data at each wavelength (A_λ), fitted to

Equation (4), where $x = [Cl_2]_{free}$ or $[Br_2]_{free}$, $p = [Cl_2]_0 = [Br_2]_0$, and l is the optical path length.

$$A_\lambda = (\varepsilon_{Br} \times l \times x) + (\varepsilon_{Cl} \times l \times x) + [\varepsilon_{BrCl} \times \lambda(2p - 2x)] \qquad (4)$$

From such data the formation constant K for the equilibrium reaction (5) [Equation (5)] was calculated to be 15.5 (1).

$$Br_2 + Cl_2 \rightleftharpoons 2\,BrCl \qquad (5)$$

The K value is 2.5 times higher in DCE than in CCl_4 and 13 times lower than in water.[9,14] This fits with the fact that an increase in solvent polarity increases the stability of the polar BrCl molecule relative to that of Br_2 and Cl_2.

Equilibrium Constant for $BrCl_2^-$ Formation

The equilibrium constant, K_1, for the reaction given in Equation (6) had previously been determined[9] spectrophotometrically in water at 25 °C on the basis of the absorbance at 343 nm of solutions of BrCl containing increasing quantities of Cl^-.

$$BrCl + Cl^- \overset{K_1}{\rightleftharpoons} BrCl_2^- \qquad (6)$$

In DCE, however, the BrCl species is much more highly dissociated than in water. The presence in these solutions of free Br_2 and Cl_2, two halogens able to react with Cl^- ions to give Br_2Cl^- and Cl_3^-, prevented the application of the spectrophotometric method reported[9] for the aqueous solutions. Although the formation of Cl_3^- anion could probably have been neglected, due to the lower stability of this species (see below) with respect to the other mixed trihalides, the presence of free Br_2 might result in the formation of Br_2Cl^- and the establishment of the multiequilibria situation shown in Scheme 1. Therefore, to obtain a preliminary estimate of the formation constant and the UV spectrum of $BrCl_2^-$ anion, this species was prepared by Cl_2 oxidation of bromide ion, through a reaction that is known[9] to be diffusion-limited, at least in water.

Recent ab initio calculations have shown[15] that the $Cl-Br-Cl^-$ species is more stable than the $Br-Cl-Cl^-$ isomer both in the gas phase and in solution, although the relative stability is affected by the solvent. Therefore, if the $Br-Cl-Cl^-$ anion were formed, it would be expected to isomerize easily, by cleavage of the $Cl-Cl$ bond, to the $Cl-Br-Cl^-$ isomer which exists in equilibrium exclusively with BrCl and Cl^-.

$$Cl_2 + Bu_4N^+Br^- \longrightarrow Bu_4N^+BrCl_2^- \qquad (7)$$

$$Cl_2 + Br^- \longrightarrow \left[Br\text{-}Cl\text{-}Cl^-\right] \longrightarrow Br\text{-}Cl + Cl^- \rightleftharpoons Cl\text{-}Br\text{-}Cl^- \qquad (8)$$

The $BrCl_2^-$ anion was therefore produced by addition of increasing amounts of tetrabutylammonium bromide (TBAB) to a DCE solution of Cl_2 in a such way as always to have the $BrCl_2^-$ species in the presence of an excess of Cl_2. The presence of an excess of Cl_2 was indeed able to reduce the dissociation of the BrCl species, in equilibrium with $BrCl_2^-$, and to avoid the establishment of the multiequilibria situation mentioned above (Scheme 1). Spectroscopic data were collected at 25 °C in the 230−420 nm range at 1.35×10^{-3} M Cl_2 and 1.35×10^{-4}−6.75×10^{-4} M TBAB. No kinetic phenomena were observed at the lower reagent concentrations and all the spectra exhibited maxima around 240 nm, attributable to the formation of $BrCl_2^-$. Assuming, therefore, the complete suppression of dissociation of BrCl eventually formed by dissociation of $BrCl_2^-$, the absorbance values at each wavelength should be the sum of the absorbances of $BrCl_2^-$, Cl_2, and possibly of BrCl:

$$A_\lambda = \varepsilon_{BrCl_2^-} \times c_{BrCl_2^-} \times l + \varepsilon_{Cl_2} \times c_{Cl_2} \times l + \varepsilon_{BrCl} \times c_{BrCl} \times l \qquad (9)$$

where:

$\varepsilon_{BrCl^2}{}^-$ and ε_{Cl^2} and ε_{BrCl} are the extinction coefficients of $BrCl_2^-$, Cl_2, and BrCl, respectively,

l is the optical path length,

$c_{BrCl^2}{}^-$ and c_{Cl^2} and c_{BrCl} are the concentrations of $BrCl_2^-$, Cl_2, and BrCl, respectively.

From Equation (9), knowing the extinction coefficients of Cl_2 and assuming that no dissociation of the $BrCl_2^-$ species had occurred under the reaction conditions (i.e., [BrCl] = 0), the molar extinction coefficients of $BrCl_2^-$ at each wavelength were calculated. Constant values of ε were found at each wavelength throughout the reagent concentration range examined. This showed that, under these conditions, only two species were present ($BrCl_2^-$ and Cl_2) and so the estimated extinction coefficients may be considered as those of the $BrCl_2^-$ species, which is characterized by an intense UV band with $\lambda_{max} = 240$ nm and $\varepsilon = 5.1\ (0.3) \times 10^4\ M^{-1}\ cm^{-1}$. The data also showed that no dissociation of the $BrCl_2^-$ species occurred even at the lower concentration examined (1.35×10^{-4} M). In order to determine the formation constant K_1, a DCE solution of $Bu_4N^+BrCl_2^-$ (analytical concentration 2×10^{-4} M), obtained by addition of TBAB to a Cl_2 solution and containing a twofold excess of Cl_2, was gradually diluted to a final concentration of around 10^{-6} M. From the spectrophotometric data, corrected for the contribution due to the excess Cl_2, it was possible to determine the degree of dissociation and evaluate the value of the formation constant $K_1 = 1.0\ (0.2) \times 10^7\ M^{-1}$.

Equilibrium Constant for Cl_3^- Formation

The UV/Vis spectra of solutions of TBACl and Cl_2 in DCE were taken in the 230−420 nm range at 25 °C, at the concentrations reported in the Exp. Sect.. An absorption band with $\lambda_{max} = 256$ nm, due to the formation of Cl_3^- anion from Cl^- and Cl_2 according to Equation (10), was apparent in solutions containing an excess of TBACl over Cl_2.

$$Cl_2 + Bu_4N^+Cl^- \rightleftharpoons Bu_4N^+Cl_3^- \qquad (10)$$

Progressive dilution of a 8×10^{-4} M Cl_2 and TBACl solution resulted in absorptions at 256 nm that did not obey the Lambert−Beer law and suggested appreciable dissociation. In order to obtain an accurate value of $K_{Cl_3^-}$ and the molar absorptivities, all the spectrophotometric measurements were fitted by NLLSQ techniques, using a previously reported[16] program, to a model describing the concentration of each possible complex A_mB_n as a function of [A] and [B]; A stands for Cl^-, B for Cl_2, and the (m,n) pair is limited to the **1**,**1** value in this approach.

$$[A_mB_n] = K_{m,n} \times [A]^m[B]^n$$

The overall "goodness of fit" was shown by the acceptably low variance value, $s^0 = 0.04$ absorbance units. The molar absorptivity at the absorption maximum [$\varepsilon_{256} = 3.5\ (0.5) \times 10^4$ M^{-1} cm^{-1}] found through the fitting procedure is in good agreement with a recently reported[17] value ($\varepsilon = 2.7 \times 10^4$ M^{-1} cm^{-1}). At variance with this, the formation constant ($K_{Cl_3^-} = 2.12\ (0.1) \times 10^3$ M^{-1}) determined in this work is moderately lower than that previously reported[17] one, $K_{Cl_3^-} = 6\ (2) \times 10^3$ M^{-1}, although this latter value was only roughly defined.

Since the reported[9] value of the formation constant of Cl_3^- from Cl_2 and Cl^- in water is 0.18, a ratio between the formation constants in the two solvents (DCE and water) of around 10^4 may be determined. This value is two orders of magnitude lower than that found for the ratio between the formation constants of Br_3^- from Br_2 and Br^- in the same solvents.[13,9] Generally, the available data indicate that the formation constant of Br_3^- is not substantially affected by the nature of the cation.[18] If this is also valid for Cl_3^-, it can be concluded that the increase in stability of the tribromide ion on passing from water to DCE is considerably higher than that of the trichloride ion. This is not surprising, since the larger Br_3^- ion would be expected to be more stabilized than Cl_3^- in a solvent incapable of electrophilic solvation, because of internal charge delocalization.

Equilibrium Constant for Br_2Cl^- Formation

In order to determine the values of the equilibrium constants K_2 and K_3, solutions containing BrCl ($[Br_2] = [Cl_2] = 3.5 \times 10^{-5}$ M) and TBACl (8.6×10^{-2} M) were mixed with equal volumes of TBAB solutions with concentrations ranging from 1.18×10^{-4} to 5.4×10^{-2} M and the UV spectra were measured in the 230−320 nm range. The observed A_λ values at each wavelength, determined in a 1 cm cell as a function of $[Br^-]$, were fitted to Equation (2) using the known[13] or previously determined values for K_1 and K_4 and for ε_1, ε_2, ε_4, ε_5, and ε_6, and a suitably adapted Newton−Raphson algorithm was used to solve K_2, K_3, and ε_3. As previously reported for the study of the same equilibria in aqueous solution,[9] subsets of data were used to determine these constants. Data obtained at low Br^- concentrations showed the disappearance of $BrCl_2^-$ and the appearance of Br_2Cl^- and so they were the best for the initial determination of K_2 and ε_3. However, data obtained at high Br^- concentrations showed the characteristic Br_3^- spectra and were most sensitive to K_3 and ε_3. The iteration started with the data at low $[Br^-]$, by optimizing K_2 and ε_3, while K_3 was assumed to be 1×10^7 M. Data at 250 nm were not used, as these were too near to the isosbestic point. The newly resolved K_2 value was used to iterate K_3 and ε_3 between 260 and 300 nm. The value of K_3 was used to reiterate K_2 and the process continued until the average K_2 and K_3 values converged. The spectra data at 240 nm were also used to reevaluate K_1. Figure 1 shows the spectra of 3.5×10^{-5} M BrCl and 4.3×10^{-2} M TBACl solutions, with $[Br^-]$ varying from 0 to 2.69×10^{-2} M. The formation constants determined in this work are summarized in Table 1 and are compared with the values previously found[9] for the same equilibria in water.

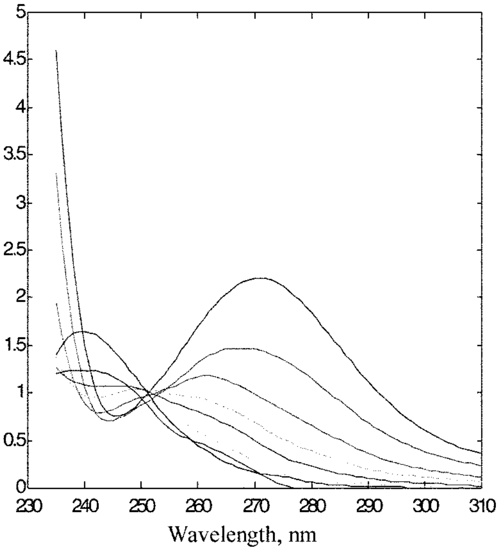


Figure 1. Spectral changes (1.00 cm cell) for solutions of BrCl ($[BrCl]_T = 3.5 \times 10^{-5}$ M) in the presence of TBACl (4.3×10^{-2} M) with variable concentrations of added Br^- ([TBAB] from 0 to 2.69 $\times 10^{-2}$ M)

On the basis of the data reported in Table 1, it can be concluded that, as expected, the stability of all the trihalide anions is considerably higher in DCE that in water. However, the disproportion reaction of Br_2Cl^- reported in Equation (11), which can be neglected in water,[9] takes place to a considerable extent in DCE. The value of $K_5 = K_1K_4/K_2K_3 = 1$ indicates that, in DCE, Br_2Cl^- is about 50% dissociated into Br_3^- and $BrCl_2^-$. The addition of an excess of Cl^- favors the formation of $BrCl_2^-$, demonstrating the impossibility of obtaining pure Br_2Cl^- in DCE solution.

$$2Br_2Cl^- \xrightleftharpoons{K_5} Br_3^- + BrCl_2^- \qquad (11)$$

Product Distribution

Stereoselectivity of BrCl, $BrCl/Cl^-$, and Br_2/Cl^- Addition

In order to compare the stereoselectivity of the electrophilic addition of BrCl with those of BrCl and Br_2 in the presence of Cl^- ($BrCl/Cl^-$ and Br_2/Cl^-), the bromochlorin-

Table 1. Formation equilibrium constants and spectroscopic data in DCE at 25 °C

Equilibrium	DCE Constant, M^{-1}	λ_{max}, nm	ε, M^{-1} cm^{-1}	Water[a] Constant, M^{-1}
$K_{Cl_3^-} = [Cl_3^-]/[Cl_2][Cl^-]$	$2.12 (0.10) \times 10^3$	256	$3.5 (0.5) \times 10^4$	0.18
$K = [BrCl]^2/[Br_2][Cl_2]$	15.5 (1)	370	122 (5)	200
$K_1 = [BrCl_2^-]/[BrCl][Cl^-]$	$1.0 (0.20) \times 10^7$	240	$5.1 (0.5) \times 10^4$	6.0
$K_2 = [Br_2Cl^-]/[BrCl][Br^-]$	$1.0 (0.20) \times 10^8$	258	$2.4 (0.2) \times 10^4$	1.8×10^4
$K_3 = [Br_2Cl^-]/[Br_2][Cl^-]$	$2.0 (0.20) \times 10^6$			1.3
$K_4 = [Br_3^-]/[Br_2][Br^-]$[b]	$2.0 (0.10) \times 10^7$	272	4.8×10^4	16.1

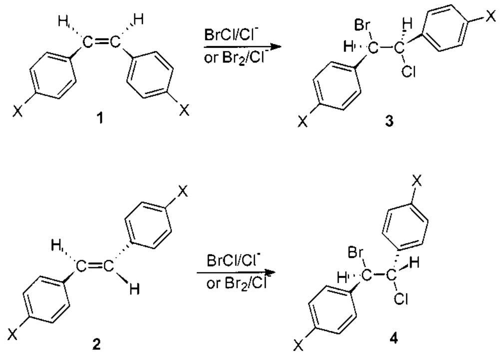
[a] From ref.[9] – [b] From ref.[13]

ation of the *cis*- and *trans*-stilbenes **1a–e** and **2a–e** in DCE at 25 °C was investigated. In the case of BrCl addition, the olefin to halogen ratio was always kept at 2:1, so that, during the reactions of olefins **1a–e**, the *cis* isomers were always in excess over the eventually formed *trans* olefins **2a–e**. In agreement with the behavior previously observed[19] for Br_2 addition to the same compounds, the formation of the *trans* olefins on treatment of the *cis* isomers may be considered as evidence of the reversible formation of the ionic intermediates. The crude reaction mixtures were analyzed by NMR and the results are reported in Table 2, together with, for the *cis* olefins, the ratio between the *trans* isomer and the addition products. The product stereochemistries were attributed on the basis of the ^3J values between the α protons found for each diastereoisomeric couple, considering the generally observed behavior of the *erythro-threo* pairs ($J_{erythro} > J_{threo}$).[20] The stability of the products under the BrCl addition conditions was checked by exposure of the pure products to solutions of BrCl at the concentrations employed. All the products were recovered quantitatively after times comparable to those required for the olefin bromochlorination, confirming that the product distributions were under kinetic control. However, the stability of the bromochlorides in the presence of TBACl was not checked since it may be inferred from the stereospecificity of these reactions. As previously reported[10] for the unsubstituted stilbenes **1b** and **2b**, the addition of BrCl and Br_2 in the presence of an excess of TBACl (four/fivefold excess in the case of BrCl and twentyfold in the case of Br_2) always gave the corresponding bromochloride arising from an *anti* stereospecific addition process, independently of the nature of the substituents on the aromatic ring and in quantitative yield. Pure *threo*-bromochlorides **3a–e** were obtained from the *cis* olefins, whereas the corresponding *trans* olefins gave the pure *erythro* isomers **4a–e**. This behavior is in agreement with the proposed[10] mechanism, involving a rate- and product-determining attack of a chloride ion on the olefin–halogen π complex.

Table 2. Product distribution for the bromochlorination of stilbenes **1a–e** and **2a–e** with BrCl in DCE at 25 °C.

			BrCl			Br_2
	Bromochlorides		Dibromides		**2**/Add. prod.	
	%	**3**:**4**	%	**5**:**6**		**5**:**6**[a]
1a	77	33:67	19		–	
2a	77	30:70	18			
1b	75	44:56	20	30:70	0.1	48:52 (18:82)[b]
2b	73	24:76	23	30:70		32:68
1c	90	43:57	<5	25:75	0.3	44:56
2c	90	25:75	<5	Nd		29:71
1d	95	42:58	<<5		0.3	42:58
1e	70	>95:<5	25	5:95	4	55:45 (5:95)[b]
2e	75	<5:>95	20	5:95		2:98

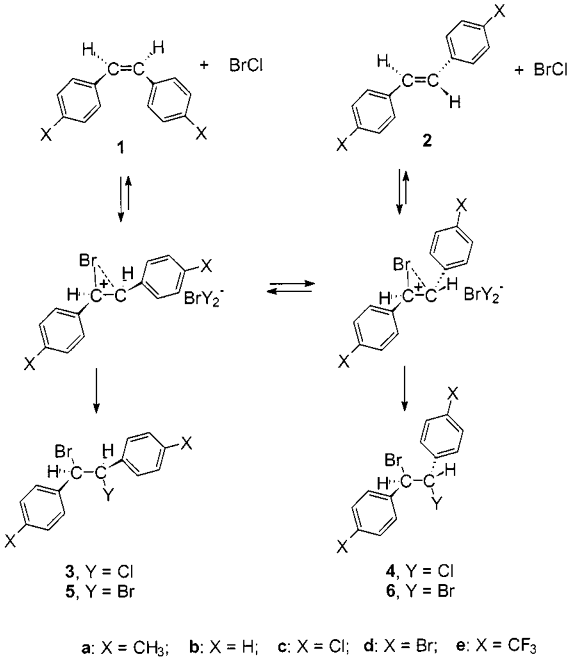
[a] From refs.[19,21] – [b] Diastereoisomeric ratio determined at very low reagent concentrations.



a: X = CH_3; **b**: X = H; **c**: X = Cl; **d**: X = Br; **e**: X = CF_3

It is noteworthy that in the case of the Br_2/Cl^- addition a larger excess of TBACl was necessary than in the case of $BrCl/Cl^-$, to avoid the formation of the corresponding dibromides. These latter probably arise from electrophilic addition of the Br_3^- species. This anion is indeed present in the Br_2/Cl^- solutions, in equilibrium with the Br_2Cl^- and $BrCl_2^-$ species (see above), and its concentration increases with increasing $[Br^-]$ during the course of the reaction. When the reactions were carried out in the presence of a fourfold excess of TBACl, significant amounts of the corresponding dibromides (ca. 15%) were detected as well as bromochlorides.

A completely different product distribution was found for BrCl addition. Firstly, it should be remarked that bromochlorides, the main products, were formed in addition to significant amounts of dibromo adducts (20–25%) and smaller amounts of dichlorides (<5%). Secondly, the reaction stereoselectivity strongly depends on the nature of the substituents on the phenyl ring, which is in agreement with the involvement of an ionic intermediate. All the results summarized in Table 2 can therefore be interpreted on the basis of the reaction sequence shown in Scheme 2.



Scheme 2

The partially bridged ions shown in this scheme may be viewed as members of a continuum connecting the extremes of open and fully closed ions, with the ions formed from the bromochlorination of **1a** and **2a** lying toward the former extreme, and those from **1e** and **2e** toward the latter. The reactions of olefins **1a** and **2a** were indeed stereoconvergent, giving an approximately 3:7 mixture of **3** and **4**, probably showing that an open β-bromocarbenium ion was involved in both cases. At variance with this, the reactions of **1e** and **2e** were highly *anti* stereospecific, in agreement with the involvement of a bridged intermediate in both cases. Finally, the two bromochlorides **3** and **4** were formed in different ratios from couples **1b**−**2b** and **1c**−**2c**, pointing to the involvement of partially bridged intermediates. With the exception of **1e**, the ratios between bromochlorides for each olefin were very similar to those between dibromides found[19,21] for Br_2 addition to the same olefins in DCE, in which the reactions were carried out at high reagent concentrations, suggesting the involvement of very similar cationic intermediates. It is noteworthy, however, that the stereochemistry of bromochlorides was in general different to that of the dibromides formed in the same reaction medium. This was more similar to the stereochemistry observed in the Br_2 addition reactions at very low reagent concentrations. In the reaction of **1e** in particular, the bromochloride had the *threo* configuration while the prevalently formed dibromide was the *meso* isomer. This behavior may be attributable to the fact that the trapping of the intermediate by chloride, or by any chloride donor species ($BrCl_2^-$ or Br_2Cl^-), occurs in a more efficient way, reflecting the higher nucleophilicity of the chloride anion with respect to bromide in the dipolar non-hydrogen bond donor DCE.[22] A shorter lifetime for the initially formed *cis* bromonium ion indeed may prevent isomerization to the more stable *trans* ion, resulting in the *erythro* (or *meso*) dihalo adduct.

Finally, as far as the formation of *trans* olefins in the BrCl addition to the *cis* isomers is concerned, it must be remarked that, in analogy with Br_2 addition,[19] this behavior was observed only with the unsubstituted olefin **1b** or with olefins bearing electron-withdrawing substituents (**1c**−**e**), or in other words when the product distribution was in agreement with the involvement of at least partially bridged intermediates, and that it may therefore be attributable to the reversion of these latter ionic intermediates to the reagents.[19] The fact that *cis*-*trans* isomerization of the starting *cis* olefin is indicative of this reversion has already been broadly discussed[19,23] for the Br_2 addition, as well as it has been more times evidenced for the Br_2 addition the relationship between bridging and return.[23,24] These latter results, however, show that the reversibility of the formation of the bromonium ions is also active in BrCl addition when the anion is mainly (see below) $BrCl_2^-$.

Kinetic Measurements. BrCl and Br_2 in the Presence of TBACl

The rates of bromochlorination by BrCl of all olefins **1a**−**e**, in the presence of a fivefold excess of TBACl, were measured spectrophotometrically in DCE at 25 °C under conditions analogous to those employed for product distribution data, by monitoring the disappearance of the electrophile ($BrCl_2^-$). The reactions followed the second order rate law of Equation (12) and the $k_{BrCl_2^-}$ values are reported in Table 3.

Table 3. Rate constants for the bromochlorination of stilbenes **1a**−**e** in DCE at 25 °C

Olefin	$k_{BrCl_2^-}$ (M^{-1} s^{-1})	k_{Br_2/Cl^-} [a] (M^{-1} s^{-1})
1a	$1.8\ (0.1) \times 10^{-2}$	$1.0\ (0.1) \times 10^{-2}$
1b	$4.6\ (0.1) \times 10^{-3}$	$3.14\ (0.1) \times 10^{-3}$
1c	$2.0\ (0.1) \times 10^{-3}$	$1.8\ (0.1) \times 10^{-3}$
1d	$1.5\ (0.1) \times 10^{-3}$	$1.0\ (0.1) \times 10^{-3}$
1e	$2.3\ (0.1) \times 10^{-4}$	$2.4\ (0.1) \times 10^{-4}$

[a] Reactions carried out at $[Br_2] = 2 \times 10^{-2}$ in the presence of a twentyfold excess of TBACl.

$$-d[BrCl_2^-]/dt = k_{BrCl_2^-}\,[Ol]\,[BrCl_2^-] \qquad (12)$$

The rate constants ($k_{BrCl_2^-}$)obtained from Equation (12) fit very satisfactorily in the log-log plot between the rate halogenation of **1a**−**e** with $BrCl_2^-$ and with Br_3^-,[13] which is characterized by a slope ($\rho = 1.1 \pm 0.04$) close to unity (Figure 2).

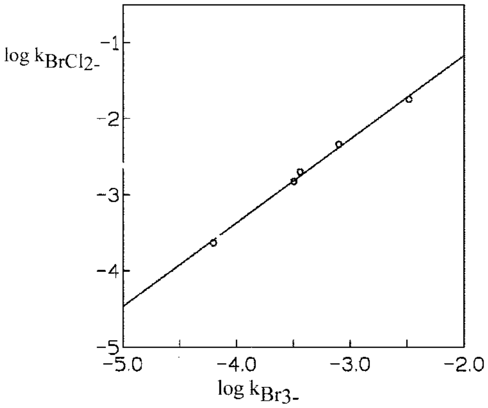
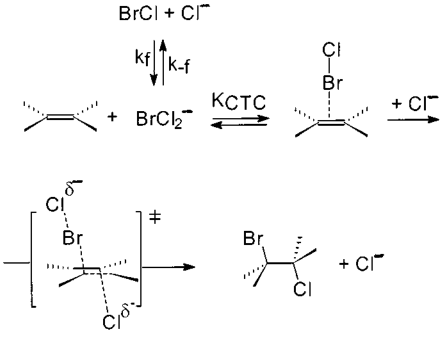


Figure 2. Comparison of the rate constants for bromochlorination and bromination of *cis*-stilbenes **1a−e** with $BrCl_2^-$ and Br_3^-, respectively

The linear correlation found between the kinetic constants $k_{BrCl_2^-}$ and $k_{Br_3^-}$, demonstrating the strict analogy in the addition mechanism of the two electrophiles, further supports the proposed[10] mechanism not involving ionic intermediates for BrCl addition in the presence of a large excess of Cl^- ions (Scheme 3).



Scheme 3

Analogously, Br_2 addition in the presence of a large excess of TBACl followed a second order rate law (first order in olefin), but the values of the kinetic constants increased with increasing chloride concentration. This behavior may be at least partially due to a salt effect. However, taking into account the equilibrium constants found in this work, it is highly probable that two different electrophiles (Br_2Cl^- and $BrCl_2^-$), reacting with very similar mechanisms but different kinetic constants, were present in solution, depending on Br_2 and Cl^- concentrations. The values of the kinetic constants k_{Br_2/Cl^-} reported in Table 3, relating to reactions carried out in the presence of a twentyfold excess of TBACl, are very similar to those found for $BrCl_2^-$ addition to the same olefins and confirm the hypothesized presence under these conditions of the same electrophilic species: mainly the $BrCl_2^-$ anion.

Finally, the rates of BrCl addition to olefins **1b**, **1c**, and **1e** in DCE were determined using either a conventional UV instrument (**1e**) or a stopped-flow apparatus (**1b−c**), by monitoring at 370 nm the disappearance of the absorption band of BrCl, in equilibrium with Br_2 and Cl_2. All reactions obeyed the third-order rate (second order in BrCl) law of Equation (13) over at least two half-lives, showing that two BrCl molecules are involved in the rate-determining step of the overall reaction.

$$-d[BrCl]/dt = k_3\,[Ol][BrCl]^2 \tag{13}$$

In order to determine the activation parameters, the kinetics of bromochlorination of olefins **1b** and **1c** were measured at different temperatures. The average third-order rate constants (k_3) are reported in Table 4, which also includes the apparent activation parameters determined from the corresponding Arrhenius plots. It is noteworthy that the k_3 values for BrCl addition are at least 6×10^2 times higher than those relating to Br_2 addition to the same olefins.

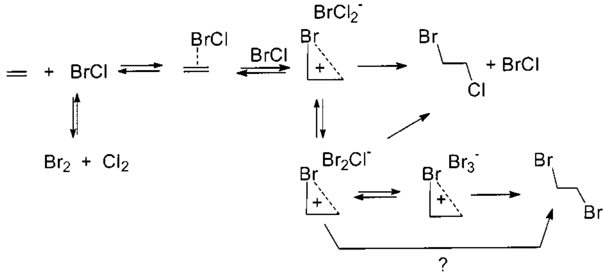
On the basis of the kinetic and stereochemical data, the electrophilic addition of BrCl to olefins in DCE may be interpreted in terms of an ionic mechanism of the type reported in Scheme 4, occurring through the initial formation of an olefin−BrCl π complex.

No spectrophotometric evidence involving the formation of a charge-transfer complex between the double bond and the halogen has been obtained in this work, due to the high absorptions of the olefins **1b**, **1c**, and **1e** in the region in which these complexes generally have their absorption maxima. However, the nearly zero or negative value of the activation energy, in analogy with Br_2 addition,[25] may be considered as indirect evidence of the involvement of one or more complexes on the reaction coordinate before the rate-determining step.[26] On the other hand, the formation of a π complex between BrCl and ethene in the gas phase has recently been detected by rotational spectroscopy.[7] Furthermore, the kinetic data suggest that ionization of the π complex is assisted by a second BrCl molecule, stabilizing the developing anion as $BrCl_2^-$. Finally, the cationic moiety of the intermediates may, depending upon the olefin structure, consist of a symmetrically or asymmetrically bridged bromonium or open β-bromocarbenium ion, and the collapse of these intermediates produces the *erythro* and *threo* bromochlorides. It is noteworthy, however, that the kinetic measurements relating to BrCl addition show that the dibromo adducts, at variance with previously reported findings,[1] cannot arise from competitive electrophilic addition of free Br_2. The lower concentration of this electrophile in solution relative to that of BrCl and the markedly lower reactivity are in disagreement with the formation of the dibromo adducts in the quantities detected in the BrCl addition reactions. This suggests that competition between dibromo and bromochloro adduct formation may be at the stage of the nucleophilic step rather than the electrophilic one. In other words, dibromides and bromochlorides might arise from attack of different anions onto the same cationic intermediate. The anion $BrCl_2^-$, arising from the ionization of the initially formed π complex, in analogy with other heteronuclear trihalide anions, is characterized[15] as having the less electronegative atom (Br) in the central position. The formation of dibromides may therefore be a con-

Table 4. Rate constants and apparent activation parameter for BrCl addition to stilbenes **1b**, **1c**, and **1e** in DCE

	T (°C)	k_3 ($M^{-2}s^{-1}$)	$E_{a,obsd}$ (kcal mol^{-1})	$\Delta H^{\neq}$ (kcal mol^{-1})	$\Delta S^{\neq}$ eu	k_{3Br_2} [a] ($M^{-2}s^{-1}$)
1b	40	$2.10\ (0.2) \times 10^5$				
	25	$2.05\ (0.2) \times 10^5$				280
	5	$1.95\ (0.2) \times 10^5$	0.36 (0.04)	-0.24	−35.5 (1)	
1c	40	$7.10\ (0.2) \times 10^3$				
	25	$1.15\ (0.2) \times 10^4$				11.5
	10	$1.30\ (0.2) \times 10^4$				
	5	$1.65\ (0.2) \times 10^4$	−3.80 (0.5)	−4.40	−55 (1)	
1e	25	6.5(0.3)				9.4×10^{-3}

[a] From ref.[19,21]



Scheme 4

sequence of the fact that the $BrCl_2^-$ ion is in equilibrium with Br_2Cl^- and Br_3^- (see above) and these latter anions are able to produce a nucleophilic Br^-.[27] It is noteworthy that the different nucleophilicities of these anions, and consequently the different lifetimes of the corresponding ion pair intermediates, may determine the different stereochemistries of bromochlorides and dibromides. Finally, as far as the much higher k_3 values found for the BrCl than Br_2 addition are concerned, it should be commented that, on the basis of the ionic mechanism reported in Scheme 4, the experimentally obtained rate constants are the products of the rate constant(s) for the slow step (the electrophilic and/or nucleophilic one) and one or two equilibrium constants for the formation of the π complex(es), according to whether only 1:1 or both 1:1 and 1:2 complexes are involved prior to bromonium ion formation. Therefore, the different reactivity may be affected: i) by the different stabilities of the olefin−halogen π complexes, ii) by the different capabilities of BrCl and Br_2 in assisting ionization, and, when the ionic intermediate formation is a reversible process, iii) by the different susceptibilities of the ionic intermediates to revert to the reagents, and iv) by the different nucleophilicities of the counteranions determining the rate of collapse to products.

Conclusions

The results of this investigation show the following:

- addition of TBACl to Br_2 solutions in DCE results in the immediate formation of more ionic species, mainly Br_2Cl^-, $BrCl_2^-$ and Br_3^-, at equilibrium. In the presence of a large excess of chloride ions, the equilibria are shifted towards $BrCl_2^-$ species, which may also be obtained by addition of a large excess of TBACl to BrCl solutions in DCE.
- The $BrCl_2^-$ anion (probably also Br_2Cl^-) reacts with alkenes as an electrophile to give the corresponding bromochloro adducts in high yield and in completely *anti* stereospecific fashion. The kinetic data, in agreement with the product distribution, confirm an addition mechanism to alkenes similar to that previously proposed for Br_3^- addition, characterized by a rate- and product-determining *anti* attack of the nucleophile (Cl^-) onto the olefin−BrCl π complex.
- BrCl addition to alkenes in DCE proceeds, analogously with Br_2 addition in the same solvent, through initial formation of a olefin−BrCl π complex, ionization of which to the ionic intermediate is catalyzed by a second halogen molecule. The nature of the intermediate cationic moiety (bridged or unbridged) mainly depends on olefin structure and determines the ability of the ionic intermediates to revert to the reagents. The counteranion, formed by BrCl-assisted ionization of the initially formed olefin−BrCl π complex as $BrCl_2^-$, is in equilibrium with Br_2Cl^- and Br_3^- species. The possibility of there being more counterions in solution, some of which are also able to give rise to nucleophilic Br^-, may explain the formation of significant amounts of dibromides in addition to bromochlorides in the BrCl addition reaction.

Experimental Section

General Remarks: ^1H and ^{13}C NMR spectra were measured with a Bruker AC 200 instrument in $CDCl_3$ containing TMS as the internal reference. − Kinetic measurements were performed with a Cary 2200 spectrophotometer or with a Tri-Tech stopped-flow instrument equipped with a diode-array detector. − Bromine (1 mL sealed ampoules, C. Erba > 99.5%), chlorine (Matheson > 99%) tetrabutylammonium bromide (Fluka, puriss. p.a.), tetrabutylammonium chloride (Fluka, puriss. p.a.), *cis*-stilbene (Aldrich, 96%), *trans*-stilbene (Aldrich, 96%) and 1,2-dichloroethane (Fluka >99.5%) were used as supplied. Substituted *cis*- and *trans*-stilbenes (**1a,c-e** and **2a,c-e**) were synthesized as previously reported.[28]

Equilibrium Measurements. Formation Constant and Molar Extinction Coefficients of BrCl: Appropriate quantities of Br_2 and Cl_2

were weighed into known volumes of DCE to prepare stock solutions, which were stored for no longer than 1 h. The concentrations of these solutions were also determined spectrophotometrically and, in the case of the Cl_2 solutions, also by iodometric titration. Suitable aliquots of the Br_2 and Cl_2 DCE solutions were withdrawn from precision microburettes and the UV/Vis spectrum of the resulting mixture (7×10^{-3} M both in Br_2 and Cl_2) was measured over the 250−500 nm range after 1: 1 dilution with the solvent, at 25 ± 0.1 °C. Aliquots of the solution (7×10^{-3} M in Br_2 and Cl_2) were mixed with equal volumes of more concentrated solutions of Br_2 or Cl_2 in order to obtained solutions characterized by an excess of one or the other halogen. The wavelengths at which the measurements were made were chosen so that the excess of the halogen would not mask absorption due to BrCl; at around 320−330 nm when bromine was in excess and between 440 and 460 nm when the halogen in excess was Cl_2. The absorbance data were then used to determine the extinction coefficients and the formation constant of the BrCl species on the basis of Equations (3) and (4), assuming complete suppression of dissociation under these conditions.

Formation Constant and Molar Extinction Coefficients of Cl_3^-: Appropriate amounts of Cl_2 and TBACl were weighed into known volumes of DCE to prepare stock solutions. The concentrations of Cl_2 solutions were also determined spectrophotometrically. Suitable aliquots of these solutions were withdrawn using precision microburettes and the UV/Vis spectra of solutions containing Cl_2 (1.5×10^{-3} to 7.6×10^{-5} M) and TBACl (1.9×10^{-2} to 7.6×10^{-5} M) were measured over the 230−420 nm range at 25 ± 0.1 °C. Computations were performed by fitting the spectrophotometric measurements to a model describing the formation of each possible complex using a NLLSQ technique, as reported in the results and discussion section.

Formation Constant and Molar Extinction Coefficients of $BrCl_2^-$: To determine the molar extinction coefficients of $BrCl_2^-$, aliquots (5 mL) of a solution of Cl_2 (2.7×10^{-3} M) in DCE were mixed with equal volumes of solution of TBAB of concentrations ranging from 2.7×10^{-4} to 1.35×10^{-3} M and the UV/Vis spectra were recorded over the 230−420 nm range at 25 ± 0.1 °C. The absorbance data were then used to determine the extinction coefficients of the $BrCl_2^-$ species, assuming complete suppression of dissociation under these conditions. To determine the formation constant of $BrCl_2^-$ anion, DCE solutions of Cl_2 ($1.25 \times 10^{-3} - 3.0 \times 10^{-3}$ M) and TBACl ($4.0 \times 10^{-4} - 1.2 \times 10^{-3}$ M) were mixed in such a way as always to have an excess of Cl_2 present, and the UV/Vis spectra were recorded over the 230−420 nm range at 25 ± 0.1 °C. All these solutions were then progressively diluted (ca. 100 times) and the absorbance data at each wavelength were used to determine the concentration of each species at equilibrium, and hence the formation constant.

Formation Constants and Molar Extinction Coefficients of Br_2Cl^-: To determine the stability constants of $BrCl_2^-$in DCE, and the related molar extinction coefficients, a stock solution of BrCl in DCE was prepared by mixing equal volumes of Cl_2 and Br_2 solutions (3.5×10^{-4} M) in the same solvent. Suitable aliquots of this solution were withdrawn using precision microburettes and were mixed with appropriate volumes of solutions of TBACl and TBAB to produce mixtures with $[BrCl]_T = 3.5 \times 10^{-5}$ M, $[TBACl] = 4.3 \times 10^{-2}$ M, and variable TBAB concentrations from 5.9×10^{-5} to 2.7×10^{-2} M. The UV/Vis spectra of these solutions were recorded over the 230−320 nm range at 25 ± 0.1 °C. Computations were performed by fitting the spectrophotometric measurements to Equation (2), as explained in the results and discussion section.

Bromochlorination Procedure and Product Analyses: DCE solutions of *cis-* and *trans*-stilbenes **1a−e** and **2a−e** (4×10^{-2} or 8×10^{-2} M) were mixed with equal volumes of solutions (4×10^{-2} M) of BrCl, of BrCl containing a four/fivefold excess of TBACl, and of Br_2 containing a twentyfold excess of TBACl. The reaction mixtures were allowed to react in the dark at 25 °C until colorless, and were then washed with water, dried, and, after solvent evaporation in vacuo, analyzed by NMR. All reactions were carried out in triplicate. The ratios reported in Table 2 and 3 were reproducible within ±2. The stability of bromochlorides **3** and **4** in the presence of halogen was checked by exposing all bromochlorides to BrCl under conditions identical to those employed in the bromochlorination reactions, monitoring by NMR. Dibromides **5** and **6** were identified on the basis of their NMR spectra.[13,19,21]

Bromochlorides 3−4: All stilbenes **1−2** were bromochlorinated as followed. DCE solutions containing 5×10^{-2} M **1a−e** or **2a−e**, 6×10^{-2} M Br_2, 6×10^{-2} M Cl_2, and 3×10^{-1} M TBACl were left at room temperature for two days. The reaction mixtures were then washed with saturated aqueous $NaHSO_3$ and water, dried, and the solvents evaporated. The residues (90−95% yield) were crystallized from chloroform to give pure bromochlorides **3−4**.

***erythro*-4a:** ^1H NMR: δ = 2.37 (s, 3 H, CH_3), 2.375 (s, 3 H, CH_3), 5.27 (d, *J* = 10.6 Hz, 1 H, CHBr), 5.35 (d, *J* = 10.6 Hz, 1 H, CHCl), 7.0−7.4 (m, 8 aromatic H). − ^{13}C NMR: δ = 21.8 (CH_3), 57.4 (CHBr), 65.7 (CHCl), 126.8, 128.2, 128.5, 129.9, 130.0 (aromatic CH) 137.0, 139.4 (quaternary aromatic C). − $C_{16}H_{16}BrCl$: calcd. H 4.98, C 59.38; found H 5.02, C 59.21.

***threo*-3a:** ^1H NMR: δ = 2.26 (s, 6 H, CH_3), 5.34 (s, 2 H, CHCl and CHBr), 6.97−7.25 (m, 8 aromatic H). − ^{13}C NMR: δ = 21.2 (CH_3) 59.5 (CHBr), 67.6 (CHCl), 127.9, 128.4, 128.7, 128.9 (aromatic CH), 129.5, 138.4 (quaternary aromatic C). − $C_{16}H_{16}BrCl$: calcd. H 4.98, C 59.38; found H 4.80 C 59.25.

***erythro*-4b:** ^1H NMR: δ = 5.25 (d, *J* = 10.5 Hz, 1 H, CHBr), 5.34 (d, *J* = 10.5 Hz, 1 H, CHCl), δ = 7.2−7.5 (m, 10 aromatic H). − ^{13}C NMR: δ = 56.5 (CHBr), 65.0 (CHCl), 126.4, 127.7, 128.0, 128.5, 128.9 (aromatic CH), 137.4 (quaternary aromatic C). − $C_{14}H_{12}BrCl$: calcd. H 4.09, C 56.88; found H 4.04, C 56.50.

***threo*-3b:** ^1H NMR: δ = 5.33 (s, 2 H, CHCl and CHBr), 7.5−7.3 (m, 10 aromatic H). − ^{13}C NMR: δ = 59.2 (CHBr), 67.5 (CHCl), 127.9, 128.1, 128.4, 128.5, 128.8 (aromatic CH), 137.3 (quaternary aromatic C). − $C_{14}H_{12}BrCl$: calcd. H 4.09, C 56.88; found H 4.24, C 56.50.

***erythro*-4c:** ^1H NMR: δ = 5.17 (d, *J* = 10.2 Hz, 1 H, CHBr), 5.27 (d, *J* = 10.2 Hz, 1 H, CHCl), 7.2−7.5 (m, 8 aromatic H). − ^{13}C NMR: δ = 55.4 (CHBr), 64.5 (CHCl), 128.4, 128.9, 129.5, 130.1 (aromatic CH). − $C_{14}H_{10}BrCl_3$: calcd. H 2.77, C 46.13; found H 2.64, C 46.55.

***threo*-3c:** ^1H NMR: δ = 5.26 (d, *J* = 7.5 Hz, 1 H, CHBr), 5.30 (d, *J* = 7.5 Hz, 1 H, CHCl), 7.0−7.2 (m, 8 aromatic H). − ^{13}C NMR: δ = 57.3 (CHBr), 66.1 (CHCl), 128.4, 129.6, 130.1 (aromatic CH); 134.**6**, 1**3**5.1, 135.5 (quaternary aromatic C). − $C_{14}H_{10}BrCl_3$: calcd. H 2.77, C 46.13; found H 2.65, C 46.45.

***threo*-3d:** ^1H NMR: δ = 5.22 (d, *J* = 7.7 Hz, 1 H, CHBr), 5.26 (d, *J* = 7.7 Hz, 1 H, CHCl), 7.0−7.3 (m, 8 aromaticH). − ^{13}C NMR: δ = 57.2 (CHBr), 66.1 (CHCl), 129.7, 130.4, 131.5 (aromatic CH), 135.6, 135.8 (quaternary aromatic C). − $C_{14}H_{10}Br_3Cl$: calcd. H 2.22, C 37.09; found H 2.21, C 36.75.

***erythro*-4e:** ^1H NMR: δ = 5.25 (d, *J* = 10.5 Hz, 1 H, CHBr), 5.37 (d, *J* = 10.5 Hz, 1 H, CHCl), 7.2−7.7 (m, 8 aromatic H). − ^{13}C

NMR: δ = 54.4 (CHBr), 63.7 (CHCl), 125.8, 126.8, 128.3, 128.6 (aromatic CH). − $C_{16}H_{10}BrClF_6$: calcd. H 2.34, C 44.53; found H 2.34, C 44.45.

***threo*-3e:** ^{1}H NMR: δ = 5.35 (d, J = 7.5 Hz, 1 H, CHBr), 5.39 (d, J = 7.5 Hz, 1 H, CHCl), 7.2−7.7 (m, 8 aromatic H). − ^{13}C NMR: δ = 56.7 (CHBr), 65.7 (CHCl), 125.3, 128.8, 129.1, 129.3 (aromatic CH), 131.2 (quaternary aromatic C). − $C_{16}H_{10}BrClF_6$: calcd. H 2.34, C 44.53; found H 2.28, C 44.85.

Kinetic Measurements: Solutions of BrCl in DCE were prepared by mixing equal volumes of equimolar solutions of suitable concentrations of Br_2 and Cl_2 in DCE. Aliquots of these solutions were added to exactly known volumes of TBACl solutions of appropriate concentration to produce a four/fivefold excess of Cl^- anions in solution. Analogously, aliquots of DCE solutions of Br_2 were added to exactly known volumes of TBACl solutions of appropriate concentration to produce a fivefold or twentyfold excess of Cl^- anion in solution. All these solutions were prepared shortly before use, were protected from daylight, and were adjusted to twice the desired initial concentrations in the kinetic runs. Aliquots of these previously thermostated solutions were mixed with equal volumes of previously thermostated solutions of olefins **1** or **2** of suitable concentrations.

The reactions of **1b** and **1c** with BrCl were carried out with a stopped-flow apparatus, those of **1e** with a conventional spectrophotometer, always monitoring the disappearance of the halogens at 370 nm. Pseudo second-order kinetics were obtained on mixing BrCl ($[BrCl]_T$ between 5×10^{-3} and 1.2×10^{-2}) with a tenfold excess of olefin. The experiments were repeated at least in triplicate and accepted on condition of a 5% maximum difference in the respective absorption/time curves. The third-order constants, obtained by fitting the absorption/time data to the appropriate integrated rate equation, are reported in Table 4. The apparent activation parameters reported in Table 4 were obtained from Arrhenius plots.

The rate constants for the bromochlorination of stilbenes **1a−e** with Br_2 in the presence of TBACl, or with BrCl in the presence of TBACl, were measured in DCE at 25 ± 0.1 °C, following halogen disappearance with the conventional spectrophotometer. Pseudo first-order kinetics were obtained on mixing Br_2Cl^- or $BrCl_2^-$ (2×10^{-3} to 5×10^{-2} M) with at least a tenfold excess of olefin. All reactions were carried out in triplicate. The kinetic constants $k_{Br_2Cl^-}$ and $k_{BrCl_2^-}$ are reported in Table 3.

Acknowledgments

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