

Intramolecular Geminal and Vicinal Element Effects in Substitution of Simple Bromo(chloro)alkenes by Methoxide and Thiolate Ions. An Example of a Single Step Substitution?

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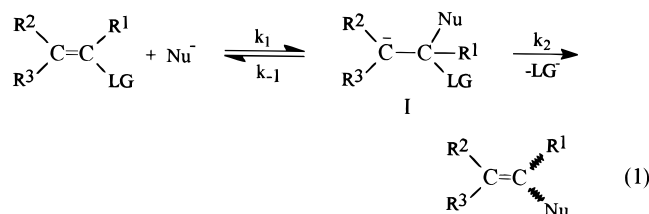
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Intramolecular element effects $k_{\text{Br}}/k_{\text{Cl}}$ for substitution of geminal bromochloroalkenes $\text{BrC}(\text{Cl})=\text{C}(\text{Br})\text{Cl}$ (**1**), $\text{BrC}(\text{Cl})=\text{CCl}_2$ (**2**), $\text{Me}_2\text{C}=\text{C}(\text{Br})\text{Cl}$ (**3**), and $\text{XCH}=\text{C}(\text{Br})\text{Cl}$ ($\text{X} = \text{Cl}$, **4**; $\text{X} = \text{Br}$, **5**), with MeO^- and RS^- nucleophiles were investigated. **3** did not give substitution, and **4** and **5** gave substitution with MeO^- via an initial elimination (to acetylene)–addition route, followed by further reactions. In reactions of **4** with thiolates, geminal element effects of 2–10 were obtained. Formation of $\text{RSC}(\text{Cl})=\text{C}(\text{Cl})\text{Y}$, $\text{Y} = \text{SR}$, Br , is ascribed to an initial halophilic reaction, followed by addition of RSCl to the formed acetylene. Reaction of **2** with MeO^- gave a high vicinal element effect, and RS^- gave a high geminal element effect. Reaction of **1** with both MeO^- and RS^- ions gave high (2 orders of magnitude) geminal element effects, which were interpreted as indicating a rate-determining $\text{C}-\text{X}$ bond cleavage. This is supported by the high $k_{\text{Br}}/k_{\text{Cl}}$ intermolecular element effects ($k(\mathbf{1})/k(\text{Cl}_2\text{C}=\text{CCl}_2)$) with MeO^- and PhCH_2S^- ions. Mechanistic alternatives based on these observations are discussed.

Introduction

Element effects (EEs)¹ studied in nucleophilic vinylic substitution ($\text{S}_{\text{N}}\text{V}$) proceeding via the addition–elimination route (eq 1) are mainly “intermolecular” EEs where



the reactivities of two systems $>\text{C}=\text{C}-\text{X}$ differing only in the nucleofuge X are compared. “Intramolecular” EEs $k_{\text{X}}/k_{\text{Y}}$, where the leaving abilities of the nucleofuges X and Y are compared in systems possessing two different leaving groups either in $>\text{C}=\text{CXY}$ (geminal intramolecular EE) or in $-\text{CX}=\text{CY}-$ (vicinal intramolecular EE), were mostly measured for $\text{X} = \text{F}$ and $\text{Y} = \text{Cl}$ or Br .² The main difference between the inter- and intramolecular EE is that, despite higher reactivities of vinyl fluorides than those of the corresponding vinyl chlorides or bromides in the intermolecular EE (i.e., $k_{\text{F}}/k_{\text{Cl}} \gg 1$),³ in geminal vinyl halides $>\text{C}=\text{C}(\text{X})\text{F}$ the heavier halogen atom is normally replaced predominantly or exclusively,^{2,4–8} though $k_{\text{F}}/k_{\text{Cl}}$ values of ca. 1 were observed for the intramolecular EE in systems $\text{CHX}=\text{CFX}$ and $\text{CX}_2=\text{CFX}$ ($\text{X} = \text{Cl}$ or Br)⁷ or $\text{R}-\text{C}(\text{F})=\text{C}(\text{F})\text{Cl}$.⁸ The

reasons for this have been discussed.⁷ We know of only two examples of an exclusive preferential substitution of the fluorine atom occurring in the reactions of $\text{PhC}(\text{F})=\text{C}(\text{F})\text{Cl}$ and $\text{EtOC}(\text{F})=\text{C}(\text{F})\text{Cl}$ with PhLi .⁹ However, these reactions apparently proceed through a different substitution route than eq 1 and include a four-center transition state, so the result is determined by the stronger $\text{Li}-\text{F}$ bond as compared with the $\text{Li}-\text{Cl}$ bond.

Despite the many available values of intermolecular $k_{\text{Br}}/k_{\text{Cl}}$ EE,^{3,10} we know of only two cases of an intramolecular geminal EE in a $>\text{C}=\text{C}(\text{Cl})\text{Br}$ system, i.e., in the reactions of 1-bromo-1-chloro-2,2-bis(*p*-nitrophenyl)ethylene or of 9-(bromochloromethylene)fluorene with thio and oxygen nucleophiles, where the values of the EE were ca. 2.0–3.2¹¹

The mechanistic significance of the element effects is that they can give information on the involvement of the $\text{C}-\text{X}$ bond cleavage in the rate-determining step (RDS) in nucleophilic vinylic substitution. For example, a high intramolecular $k_{\text{Br}}/k_{\text{Cl}}$ EE will indicate that the RDS involves a $\text{C}-\text{X}$ bond cleavage step, either in the rare (or unknown) single step process¹² or in a second slow $\text{C}-\text{X}$ bond cleavage step (k_2) from the intermediate carbanion

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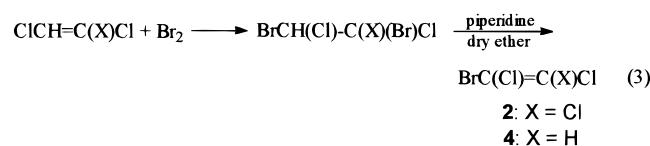
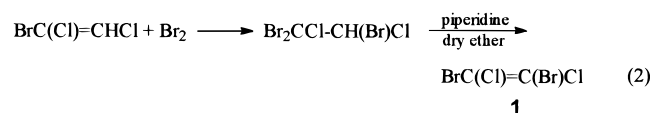
(I) formed in the first step (k_1) of a multistep process (eq 1). An intramolecular EE close to unity will indicate either a rate-determining k_1 or that the transition state for the C–X bond cleavage step k_2 is early.

The goal of the present work is to use this probe in order to extend our previous mechanistic studies on systems of relatively low reactivity, the polyhaloethylenes, where a C–X bond cleavage may be involved in the RDS. An experimental problem is that polysubstitution can distort the product ratios. However, in the substitution of polychloroethylenes with sodium phenolate and benzenethiolate in dipolar aprotic solvents,¹³ it was found that substitution of one or more chlorine atoms can take place depending on the reaction conditions. This and our previous finding that monosubstitution can occur if low nucleophile concentrations are used and the reaction is monitored at early reaction times enabled us to overcome this difficulty.¹¹

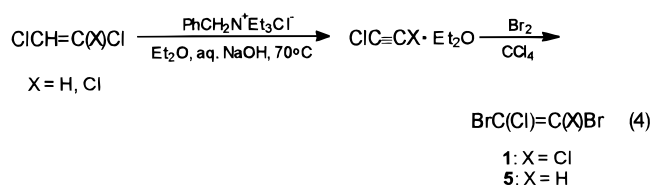
Results

Two types of compounds were investigated: (a) alkenes lacking a vinylic hydrogen, such as $\text{BrC}(\text{Cl})=\text{C}(\text{Br})\text{Cl}$ (**1**), $\text{Cl}_2\text{C}=\text{C}(\text{Br})\text{Cl}$ (**2**), and $\text{Me}_2\text{C}=\text{C}(\text{Br})\text{Cl}$ (**3**), where competition from elimination–addition pathways is not a problem and (b) trihaloethylenes bearing a vinylic hydrogen, i.e., $\text{ClCH}=\text{C}(\text{Br})\text{Cl}$ (**4**) and $\text{BrCH}=\text{C}(\text{Br})\text{Cl}$ (**5**), where substitution via an elimination–addition route is a mechanistic option. The nucleophiles used were sodium methoxide in the dipolar aprotic solvents acetonitrile and DMF, and sodium thiolates in acetonitrile.

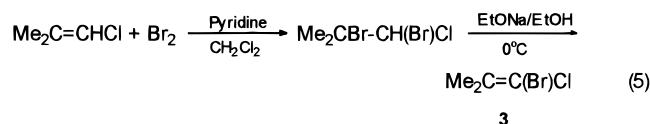
Synthesis. Chlorobromoethylenes **1**, **2**, and **4** were prepared by bromination/dehydrobromination sequences of dichloro- and trichloroethylenes according to eqs 2 and 3:



Compound **1** was also prepared by Pielichowski's method (eq 4)¹⁴ which was also used to obtain compound **5**:



Compound **3** was prepared from 1-chloro-2-methylpropene according to the method of Cunico and Han (eq 5):¹⁵



Compounds **1**, **4**, and **5** were obtained as mixtures of the *Z* and *E* isomers. The isomeric ratio for **1** prepared according to eq 2 was 3:4 based on the ¹³C NMR spectrum that displayed two signals at 108.05 and 107.21 ppm. The assignment was based on comparison of the ¹³C NMR spectrum of **1** with that of its bromofluoro analogue for which the *E* and *Z* isomers were assigned on the basis of the F–F couplings on the ¹³C satellites.² The ¹³C NMR spectrum of $\text{BrC}(\text{F})=\text{C}(\text{Br})\text{F}$ displayed two signals in a ca. 25:75 ratio: the *Z* isomer at 128.51 ppm with ¹ $J(^{13}\text{C}-\text{F})$ 324.2 Hz and ² $J(^{13}\text{C}-\text{F})$ 34.8 Hz and the main *E* isomer at 123.58 ppm with ¹ $J(^{13}\text{C}-\text{F})$ 252.8 Hz and ² $J(^{13}\text{C}-\text{F})$ 103.0 Hz. Their ratio resembles that of 21:79 determined from the ¹H NMR spectrum of $\text{BrCH}=\text{C}(\text{Br})\text{F}$.¹⁶ Hence, we conclude that the downfield and upfield signals in the ¹³C spectra of $\text{BrCX}=\text{C}(\text{Br})\text{X}$ for both X = F and X = Cl belong to the *Z* and *E* isomer, respectively. The chemical shifts difference $\Delta\delta(Z-E)$ between the isomers should decrease on decreasing the difference in electronegativity of the geminal substituents. Indeed, for $\text{BrC}(\text{F})=\text{C}(\text{Br})\text{F}$ and for **1** $\Delta\delta(Z-E) = 5$ and 1 ppm, respectively. Therefore, the *E:Z* ratio for **1** is 4:3. When compound **1** was prepared by bromine addition to dichloroacetylene (eq 4) the *E:Z* ratio was 11:1, as was expected from a predominant *trans*-addition to the acetylene.

For compound **2** the ¹³C NMR spectrum displayed two signals at 106.14 and 121.83 ppm, corresponding to the CClBr and CCl_2 groups, respectively.¹⁷

The two vinylic carbons of compound **3** appear in the ¹³C NMR spectrum at 134.72 (CClBr) and 100.02 (CMe_2) ppm and the two methyl groups at 24.21 and 21.62 ppm. In the ¹H NMR spectrum the two methyl groups appear at 1.89 ppm due to accidental isochronicity.

In the ¹H NMR spectrum of **4** two isomers are observed in a 4:5 ratio. The more intense signal is at 6.70 ppm and the less intense one is at 6.60 ppm. Their assignment to the *Z* and *E* isomer, respectively, is based on an additivity scheme¹⁸ [calculated to be 7.02 (*Z*) and 6.71 (*E*) ppm]. In the ¹³C NMR spectrum the signals were at 111.14 (CClBr) and 122.35 ppm (CHCl) for *Z*-**4** and 108.18 (CClBr) and 120.54 ppm (CHCl) for *E*-**4**.

For compound **5**, the two signals in the ¹H NMR spectrum at 7.08 and 6.76 ppm in a 1:2 ratio were assigned by analogy to the *Z* and *E* isomers, respectively.

Reactions of the Methoxide Ion. With 1. The reaction of 0.02 M **1** with an equimolar amount of MeONa in 50 mL of DMF at 100 °C for 5 h was slow, giving only 7% conversion. GC–MS analysis showed that the main product is a $\text{Cl}_2\text{BrC}_2\text{OMe}$ isomer showing a cluster of base peaks (lower one at m/z 204; throughout this paper we will give only the lowest m/z values for a cluster of peaks for isotopomeric species) with the proper isotopic distribution for the monobromo substitution product. The ¹H NMR spectrum of the reaction mixture after water–chloroform workup showed two MeO signals at δ 3.64 and 3.76 ppm in a 2:1 ratio, indicating formation of the *Z/E* mixture of $\text{BrC}(\text{Cl})=\text{C}(\text{Cl})\text{OMe}$ (**6**). As with **4** and **5** (see below), no trace of the chlorine displacement product, i.e., $\text{Br}_2\text{ClC}_2\text{OMe}$, nor any other substitution product was

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detected by GC–MS. When the reaction was carried out in MeCN, the only products were again *E*-**6** and *Z*-**6**, displaying the same ¹H NMR and GC–MS signals as those formed in the reaction in DMF, although a substantial resinification also took place.

With 2. In the reaction of 0.02 M **2** with 0.02 M MeONa in 50 mL of DMF at 100 °C for 5 h unreacted **2** was recovered in addition to four additional species which were identified by GC–MS and NMR spectra:

(1) The ortho ester ClCHBrC(OMe)₃ [MS: *m/z* 201 (21, M – OMe), 105 (46, C(OMe)₃). ¹H NMR δ (CDCl₃): 6.02 s (1H, CH), 3.45 s (9H, Me)], formed in ca. 1% yield [The analogous Cl₂CHC(OMe)₃ is known. ¹H NMR δ (CDCl₃): 5.75 (CHCl₂), 3.45 (OMe).⁷]; (2) trichloroethylene [¹H NMR δ (DMF-*d*₆): 6.45], formed in traces; (3) *E*- and *Z*-BrC(Cl)=C(Cl)OMe (**6**) (the same ¹H NMR signals as in the reaction of **1**), formed in <1% yield; and (4) ClCH=C(Cl)OMe (**7**) [¹H NMR δ (CDCl₃): 5.47 (1H, =CH), 3.78 (3H, Me) (lit.⁷ 5.45 and 3.78)], formed in <1% yield.

The reaction in MeCN was much faster even though it took place at a lower temperature and for a shorter period (80 °C, 1 h), and it gave 44% of unreacted **2** and four additional species whose percentages are given below on the basis of their uncalibrated integration values:

(1) trichloroethylene ClCH=CCl₂ [*m/z* 130 (100, M), 95 (100, M – Cl), 60 (43, M – 2Cl)], formed in 42%; (2) ClCH=C(Br)Cl (**4**) [*m/z* 174 (43, M), 139 (5, M – Cl), 95 (100, M – Br)], formed in 9% yield; (3) ClCH=C(Cl)OMe (**7**) [*m/z* 126 (M), overlapped with trichloroethylene], formed in 3% yield; and (4) dichloroacetylene ClC≡CCl (**8**) [*m/z* 94 (100, M), 59 (15, M – Cl), 47 (11, CCl)], formed in 2%.

With 4. The reaction of **4** with a suspension of an equimolar amount of MeONa in MeCN proceeds exothermally at room temperature. The reaction mixture was analyzed after 1 h by GC–MS and gave several compounds. The main peak (75% by uncalibrated GC) consisted of the overlapped peaks of unreacted **4** and the monobromo substitution product, ClCH=C(Cl)OMe (**7**) (for C₃H₄³⁵Cl₂O *m/z* 126, M). The ¹H NMR spectrum of isolated **7** displayed only two signals at δ (CDCl₃) 3.74 (MeO) and 5.43 (=CH) ppm (lit.⁷ 3.78 and 5.45 ppm), suggesting that only a single geometrical isomer was formed. Likewise, the ¹³C NMR spectrum displayed only three signals at 58.50 (OMe), 97.0 (=CHCl), and 144.65 (=CCl) ppm. These data are insufficient for distinguishing between the *Z* and *E* isomers of **7**, and the structure was not assigned in the literature either.⁷ The ¹H NMR spectrum of the crude reaction mixture showed a *Z*-**4**:*E*-**4** ratio of 37:63, lower than the 45:55 ratio for the precursor, indicating that the *Z* isomer reacted faster.

In addition to **7** and **8**, five more compounds were detected and identified by GC–MS and ¹H NMR:

(1 and 2) methyl chloride (**9**) [*m/z* 50 (100, MeCl)] and methyl bromide (**10**) [*m/z* 94 (50, MeBr), 79 (5.3, Br)]; the two overlapping peaks consisted 10% of the observed intensity]; (3) methyl chloroacetate (ClCH₂COOMe, **11**) [¹H NMR δ (CDCl₃): 3.72 (Me), 4.11 (CH₂)], formed in 3% yield; (4) methyl dichloroacetate (Cl₂CHCOOMe) [*m/z* 127 (100, M – Me), 113 (78, M – CO – H), 95 (32, C₂HCl₂), 49 (73, CH₂Cl). ¹H NMR δ (CDCl₃): 3.84 (Me), 5.94 (CH) (lit.⁷ 5.97, 3.89).], formed in 2% yield; (5) BrC(Cl)=C(Cl)OMe (**6**) [*m/z* 204 (31, M), 161 (69, CCl₂Br)], as traces; and (6) compound **1** [*m/z* 252 (32, M), 173 (60, M – Br), 138 (14, M – Br – Cl), 94 (46, M – 2Br), 79 (13, Br), 59 (26, M – 2Br – Cl)], formed in 4% yield.

Table 1. Reaction of Excess 1,2-dibromo-1,2-dichloroethylene (1) with RSNa in MeCN^a

product	R = PhCH ₂ ^b	R = PhCH ₂ ^c	R = Me
ClC(Br)=C(Br)Cl ^d	72.4	47.4	91.3
Cl ₂ C(Br)CH(Br)Cl ^e		11.8	
RSC(Cl)=CHCl	3.2	7.1	
RSC(Cl)=C(Br)Cl	7.7	25.6	4.3
RSSR	13.3	8.1	

^a Numbers given are relative uncalibrated GC intensities. ^b **1** was prepared according to eq 2. ^c **1** was prepared according to eq 4. ^d Also detected were 2.5 ± 0.3% of Br₂C(Cl)CH(Br)Cl (the precursor to **1**) and 1.4 ± 0.2% of Br₂C=C(Br)Cl (its HCl elimination product) which were not detected by NMR of precursor **1**, although they are presumably present in it in minor percentage. ^e Presumably formed by addition of Br₂ to trichloroethylene, which is the first precursor to **1** in eq 4.

Table 2. Reaction of Excess 1-Bromo-1,2,2-trichloroethylene (2) with RSNa in MeCN^a

product	R = PhCH ₂	R = Me
Cl ₂ C=C(Br)Cl	39.6	92
ClC(Br)=C(Br)Cl ^b	2.4	1.1
RSC(Cl)=CHCl	8.3	
RSC(Cl)=CCl ₂	9.9	0.8
RSC(Cl)=C(Br)Cl	31.0	6.1

^a Numbers given are relative uncalibrated GC intensities. ^b Presumably formed in a small quantity by elimination of HCl rather than HBr from precursor BrCl₂CCH(Cl)Br.

When the MeONa was dried for 2 days under high vacuum and the mixture was protected from moisture, the GC–MS of the crude reaction mixture showed (apart from unreacted **4**) a large peak of dichloroacetylene (**8**) and only a small peak of **7**. In the ¹³C NMR coupled spectrum a singlet at 49.23 ppm, assigned to dichloroacetylene, was observed (calculated δ¹³C 53 ppm).

With 5. In the reaction of 1,2-dibromo-1-chloroethylene **5** with MeONa in DMF, no substitution products were formed as judged from the lack of MeO signals in the 3–4 ppm region in the ¹H NMR spectrum of the crude reaction mixture. In contrast, in the reaction in MeCN, seven singlet signals were observed between 3.4 and 3.9 ppm, five of them at 3.43, 3.48, 3.76, 3.86, and 3.89 were small (5, 6, 6, 8, and 12%, respectively) and the two most intense ones were at 3.60 (30%) and 3.84 (33%) ppm. We ascribe the signals at 3.84 and 5.99 ppm to the ester ClBrCHCOOMe and the pair of signals at 3.60 and 5.2 ppm to the monobromo substitution product BrCH=C(Cl)OMe. When starting from a 1:2 *Z*-**5**:*E*-**5** ratio, the only isomer observed at the end of the reaction was *E*-**5**, indicating that the reactivity of the *Z* isomer was much higher than that of *E*-**5**.

Reactions with Thiolate Ions. Chlorobromoethylenes **1–5** in 8-fold molar excess were reacted with methyl, *tert*-butyl, and benzyl thiolate ions (RS[–], R = Me, *t*-Bu, PhCH₂) under argon at room temperature in MeCN for 24 h. These conditions ensure that only monosubstitution takes place at early reaction percentage, when product composition was determined. Analysis was mainly conducted by GC–MS, but ¹³C and ¹H spectra were also recorded when appropriate. The results for **1**, **2**, **4**, and **5** are summarized in Tables 1–4. The results for tri- and tetrachloroethylenes are given in Tables 5 and 6. The reaction of **3** at 78 °C with MeS[–] for 18 h or with PhCH₂S[–] for 23 h did not give any substitution product.

1 vs Tetrachloroethylene External Element Effects. Because of expected complications due to the low

Table 3. Reaction of Excess 1-Bromo-1,2-dichloroethylene (4) with RSNa in MeCN^{a,b}

product	R = <i>t</i> -Bu	R = Me	R = PhCH ₂ ^c
ClCH=C(Br)Cl	58.9	31.5	8.1
RSCH=CHCl	0.4	<i>d</i>	3.2
RSC(Cl)=CHCl	4.8	5.8	17.5
RSC ₂ H(Br)Cl ^e	2.3	45.5	4.0
RSC(Cl)=C(Br)Cl	16.3	12.9	13.1
RSC(Cl)=C(Cl)SR		2.4	3.0
RSSR	17.3		29.3

^a Numbers given are relative uncalibrated GC intensities. ^b The precursor contains traces of BrCH=C(Br)Cl. ^c 3.5% of an unidentified compound was also present. Its highest *m/z* was 147, it contained no halogen, and it showed a C₇H₇⁺ signal. It may be PhCH₂SC≡CH (*m/z* 148) which by loss of H gives an *S*-benzylthiurium ion (*m/z* 147), which is a known MS fragment. ^d The retention time is identical with that of **4**, so that separate integration is impossible. ^e Two compounds of this composition with different retention times were observed in the GC-MS for R = Me and PhCH₂. For R = Me, in the mass spectrum of the first eluted compound (2.8%) there are fragments at *m/z* 125 and 127 in 1:1 ratio which are consistent with the fragment [CSBr]⁺. These do not appear in the spectrum of the second compound (42.7%) which showed a 1:1 ratio of *m/z* 126 and 128, which are consistent with the fragment [MeSBr]⁺. Both spectra display 1:1 ratio of signals at *m/z* 136 and 138, belonging to [C₂HSBr]⁺ formed by loss of Me and Cl from vicinal carbons. The first eluted compound was tentatively assigned as RSC(Br)=CHCl, and the second one was assigned as RSCH=C(Br)Cl.

Table 4. Reaction of Excess 1,2-Dibromo-1-chloroethylene (5) with PhCH₂SNa in MeCN^a

product ^b	percent	product ^b	percent
BrCH=C(Br)Cl	22	PhCH ₂ SC(Br)=CHCl	4
PhCH ₂ SCH=CHCl	18	PhCH ₂ SCH ₂ Ph	7
PhCH ₂ SCH=CHBr	6	PhCH ₂ SSCH ₂ Ph	37
PhCH ₂ SC(Cl)=CHCl	3		

^a Numbers given are relative uncalibrated GC intensities. ^b 3% of an unidentified compound was also present. It displayed the highest *m/z* at 210, contained no halogen, and showed a C₇H₇⁺ signal.

Table 5. Reaction of Excess Trichloroethylene with MeSNa in MeCN^a

product	percent	product	percent
MeSC(Cl)=CHCl	50.3	MeSCH=C(Cl)SMe	3.5
MeSCH=CCl ₂	38	(MeS) ₂ C=CHCl	8.0

^a Numbers given are relative uncalibrated GC intensities.

Table 6. Reaction of Excess Tetrachloroethylene with RSNa in MeCN^{a,b}

product	R = <i>t</i> -Bu	R = Me	R = PhCH ₂
Cl ₂ C=CCl ₂	80	25.1	
RSC(Cl)=CHCl	7.3	<0.1	
RSC(Cl)=CCl ₂	3.3	67.6	<i>c</i>
(RS) ₂ C=CCl ₂ ^d or RSC(Cl)=C(Cl)SR ^d		1.3 or 5.6	
RSSR	9.5		

^a Numbers given are relative uncalibrated GC intensities. ^b The mixture was evaporated and the remainder was analyzed. ^c Main product. Isolated. ^d Two products with the same *m/z* were formed and were not identified.

solubility of the nucleophile and the possible formation of multisubstitution products, the rates of the reactions of **1** and tetrachloroethylene required for calculation of "external" EE were not measured separately but in the mixture of the two tetrahaloalkenes. The reactions of mixtures of **1** and tetrachloroethylene were carried out by dissolving together 5 mmol of each substrate in 1.5–2 mL of MeCN and adding 10 mmol of dry MeONa or PhCH₂SNa at room temperature and the reactions were

Table 7. Reaction of a 1:1 Mixture of 1,2-Dibromo-1,2-dichloroethylene (1) and Tetrachloroethylene with MeONa in MeCN (in percents relative to MeCN)

no.	time (min)	C ₂ Cl ₄	1	6	EE
1	0	21.8	20.2		
2	1	19.9	13.3		3.9
3	8.3	20.1	8.5	2.9	7.4
4	15.5	20.2	6.8	4.0	9.0
5	22.7	20.1	6.7	4.2	8.6
6	30	20.1	6.6	4.3	8.6
7	37	21.0	6.1	5.1	8.5
8	45	20.5	6.3	4.8	11.5
9	67	20.4	6.8	4.5	10.3
10	89	20.6	6.8	4.6	12.1
11	102	20.5	6.6	4.6	11.3

Table 8. Reaction of 1:1 Mixture of 1,2-Dibromo-1,2-dichloroethylene (1) and Tetrachloroethylene with PhCH₂SNa in MeCN (in percents relative to MeCN)

no.	time (min)	C ₂ Cl ₄	1	EE
1	0	45.4	36.5	
2	1.5	43.4	20.5	9.9
3	5.7	43.4	12.3	15
4	11.5	43.3	12.4	14.2
5	17.1	42.1	12.9	8.9
6	23.4	41.8	13.0	8.1

followed by GC. The results are presented in Tables 7 and 8, along with the calculated values of the intermolecular EE for each point. In Table 7 the percentage of a newly formed compound, which was shown by GC-MS to be compound **6**, is also given. It is evident from these data that the content of the two substrates decreased with time at sharply different rates, the main changes occurring in the first several minutes for both nucleophiles. Values of the intermolecular *k_{Br}/k_{Cl}* EE calculated from eq 6,

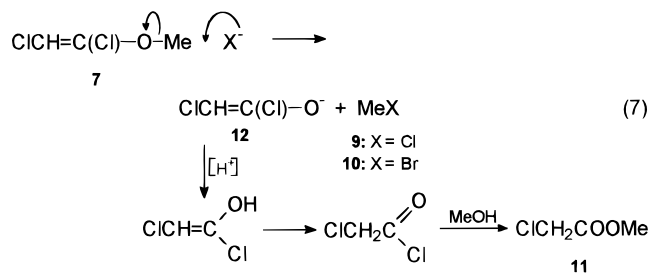
$$EE = \frac{[\mathbf{1}]_0 - [\mathbf{1}]_t}{[\mathbf{1}]_0} \frac{[\mathbf{C}_2\text{Cl}_4]_0 - [\mathbf{C}_2\text{Cl}_4]_t}{[\mathbf{C}_2\text{Cl}_4]_0} \quad (6)$$

are rather sensitive to small variations of the percentage of tetrachloroethylene and, hence, should be regarded as a reasonable approximation. Nevertheless, we can conclude that, despite the large error obtained in averaging the individual points for the EE, the intermolecular EEs are the highest values obtained so far, being 9.1 ± 1.7 with MeO⁻ and 11.2 ± 2.7 with PhCH₂S⁻.

Discussion

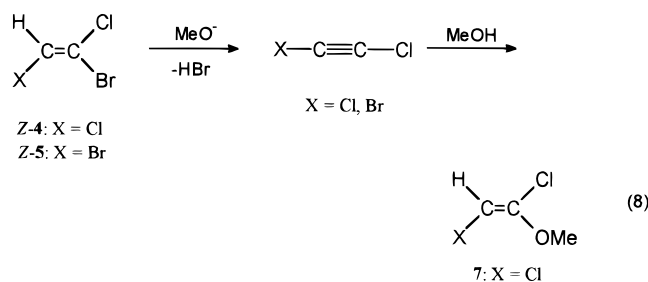
The reactions of the polyhaloethylenes studied here with the oxygen and sulfur nucleophiles demonstrate again "the rich mechanistic world of nucleophilic vinylic substitution".¹⁹ The outcome of a crowded array of mechanistic routes is that small structural variations can lead to elimination-addition (E-A), nucleophilic addition-elimination (Ad_N-E), and halophilic reactions, taking place either exclusively or competitively for the different substrates. Moreover, the initial products frequently react further under the reaction conditions, leading to products which could be a posteriori rationalized but not necessarily predicted, as demonstrated below.

Reactions of 1-Bromo-1,2-dichloroethylene 4 and 1,2-Dibromo-1-chloroethylene 5. (a) **Reactions with MeONa.** The formation of both MeCl and MeBr (**9** and **10**) in reaction of **4** with MeONa is reminiscent of the formation of dimethyl ether in the reaction of BrC(F)=C-(Br)F with MeONa.² In the absence of a nucleophilic methyl anion source, **9** and **10** should be secondary products derived from the initially formed species. The most plausible route for their formation is a reaction between the two products formed in the initial substitution reaction, i.e., an S_N2 attack of Cl⁻ or Br⁻ on the methoxydebromo substitution product **7** (eq 7).



Although ethers are usually stable to reactions with nucleophiles, the increased electrophilicity of the methyl group in **7** due to electron withdrawal by the dihalovinyl moiety is apparently responsible for the reaction with X⁻. Furthermore, the other reaction product, i.e., the vinyloxy anion **12**, is protonated and by a further ketonization and methanolysis affords methyl chloroacetate **11** which was identified by ¹H NMR spectroscopy.

Substitution of **4** with MeO⁻ to form **7** apparently proceeds by an elimination–addition pathway, as proved by the almost exclusive formation of dichloroacetylene **8** under especially dry conditions. The *Z* isomers of trihaloethylenes **4** and **5** are more reactive than the *E* isomers toward MeONa, as judged by the increase in the percentage of the *E* isomers (from ¹H NMR) in the recovered unreacted precursor after the substitution. Since a base-promoted elimination of HBr is faster than elimination of HCl, and hydrogen and bromine are situated trans in the *Z* isomer, this finding corroborates an elimination as the first step in the reaction. Trans addition of MeOH across the formed triple bond of dichloroacetylene formed from **4** or bromochloroacetylene formed from **5**, respectively, affords the observed ether product **7** (eq 8). In addition to the evidence based on the relative reactivity of the *E* and *Z* isomers, the presence of a strong base, and the exclusive formation of **8** under dry conditions, corroborating evidence for the formation of the explosive dichloroacetylene in the elimination step of the E–A route is the fact that even when the MeONa was not especially dried, the reaction mixture sometimes exploded when heated in air, and it had the typical smell of haloacetylene.



Consequently, the reactions of **4** and **5** can not provide data on the intramolecular EE in the Ad_N–E route.

(b) **Reactions with Thiolates.** The reaction of trichloroethylene with MeS⁻ which gives both *E*- and *Z*-ClCH=C(SMe)Cl and Cl₂C=CHSMe is likely to proceed via the Ad_N–E route rather than by an exclusive E–A route, which should give only ClCH=C(SMe)Cl. We reasonably assume that **4** and **5** will react similarly since an E–A route will give only ClCH=C(SMe)Cl in the case of **4**. The Ad_N–E reaction of *E/Z*-**4** with the three thiolate nucleophiles RS⁻ (Table 3) could give a priori three *E/Z* pairs derived from substitution. For the reaction of **4** with *t*-BuS⁻ and MeS⁻, both a bromine replacement product and a single chlorine replacement product were formed. With PhCH₂S⁻, a bromine replacement and two chlorine replacement products were observed, one of which was <1% of the other. Whereas the bromine replacement product should be RSC(Cl)=CHCl if no rearrangement takes place, the single chlorine replacement product (or major one with PhCH₂S⁻) can be either RSC(Br)=CHCl (**13**) or RSCH=C(Br)Cl, depending on the regiochemistry of attack of the nucleophile. This raises the question if the measured element effect is geminal or vicinal.

Although the products were not isolated and our information is derived from GC–MS, we believe that the chlorine replacement product is **13** for the following reason. The observed *k*_{Br}/*k*_{Cl} element effects are 2, 2, and 10, for reaction with *t*-BuS⁻, MeS⁻, and PhCH₂S⁻, respectively, i.e., the element effect increases with the increased softness of the nucleophile. We calculated by AM1 the distribution of the LUMO of **4** and found that only 6% of it is localized on the β-carbon (CHCl), while 35% is localized on the α-carbon (CClBr).²⁰ As reactions of soft nucleophiles should be governed by orbital rather than by charge control, the reaction at the α-carbon should predominate. In this case, the element effect is geminal.

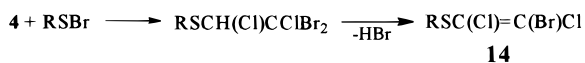
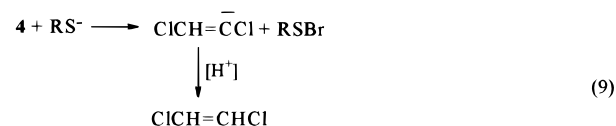
An intriguing process in the reaction of trihaloalkene **4** with all the three thiolate ions is the formation in substantial amounts of the tetrasubstituted trihalovinyl sulfides, RSC(Cl)=C(Br)Cl (**14**) (Table 3). Together with their further substitution product RSC(Cl)=C(Cl)SR, R = Me, PhCH₂, they consist of ca. 16% of the total substitution product. This can be rationalized in three ways. (i) A partial disproportionation of **4** to dihalo- and tetrahaloethylene, with a subsequent substitution of the latter. This route requires the formation of comparable amounts of products with two vicinal vinylic hydrogens to those of the tetrasubstituted alkenes. Such products were not formed, except for only 0.4–1.1% of chlorovinyl sulfides RSCH=CHCl. However, since dichloroethylene is volatile, some of it may be lost from the reaction mixture before the reaction with the RS⁻. Consequently, the theoretically expected 1:1 ratio of the disubstituted to tetrasubstituted alkenes may be changed in favor of the latter. (ii) An Ad–E process, initiated by addition of disulfides RSSR (formed as side products in our reaction) to **4** followed by elimination of a hydrogen halide molecule. This route have precedents in the addition of disulfides^{21–24} or their R₂S⁺SR⁻·2,4,6-(NO₂)₃C₆H₂SO₃⁻ salts²³ to both simple and functionalized alkenes. Base-cata-

(19) Rappoport, Z. *Recl. Trav. Chim. Pays-Bas*. **1985**, *104*, 309.

(20) AM1 calculations were performed by using the MOPAC program with full geometry optimization.

(21) Holmberg, B. *Arkiv Kemi, Mineral., Geol.* **1939**, *13B*, 6 (*Chem. Abstr.* **1940**, *34*, 2341⁹).

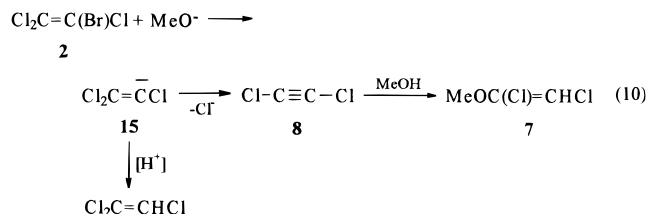
lyzed addition of disulfides to acetylenes²⁵ and perfluoroacetylenes²⁶ is also known as well as the formation of trichlorovinyl sulfides RSC(Cl)=CCl₂ in the reaction of trichloroethylene with disulfides under free-radical conditions.²⁷ The iodine-catalyzed addition of disulfides to styrenes^{21,22} implicates sulfenyl iodides RSI as the reactive intermediates. This raises the most likely route (iii) of sulfenyl bromide addition to **4**. The sulfenyl bromide may arise by a halophilic attack of RS⁻ on the bromine atom of **4**. We therefore tentatively present the formation of trihalovinyl sulfides RSC(Cl)=C(Br)Cl **14** in the reaction of **4** with thiolate ions by the sequence of steps of eq 9. Note, however, that the reservation raised concerning the product ratio in route (i) applies here too.



Reactions of Bromotrichloroethylene 2. In the reactions of the tetrasubstituted **2** there is a regioselectivity problem since attack can take place on either of the two different sites, the =C(Cl)Br (C_α) and =CCl₂ (C_β). If the attack is on C_α, the measured element effect will be an intramolecular geminal element effect, while when it takes place at both C_α and C_β, both intramolecular geminal and vicinal effects will be obtained.

The reaction of **2** with MeO⁻ in DMF, which gives products that retained bromine, i.e., the *Z* and *E* isomers of **6** as well as its further reaction product, the ortho ester BrCHCIC(OMe)₃, indicates that the nucleophilic attack takes place on the =CCl₂ rather than on the =C(Cl)Br group. This is consistent with the results of the AM1 calculations which showed that the electron density on C_β (-4.079) is 0.13 e lower than on C_α (-4.210).²⁰

The other two products lack bromine, but they are not the simple bromine replacement products since they contain a vinylic hydrogen. They are most likely formed by a bromophilic reaction of the MeO⁻ on **2**, forming carbanion CCl₂=CCl⁻ (**15**), which is then protonated to trichloroethylene, i.e., by a stepwise reduction. The main product in the reaction in MeCN, which is trichloroethylene, seems also to be formed similarly. Its further substitution gives **7**. The trichlorovinyl carbanion **15** can also expel a chloride ion, thus accounting for the formation of the observed dichloroacetylene (eq 10).



The second most abundant product is 1-bromo-1,2-dichloroethylene **4**, which is most likely formed by a

chlorophilic MeO⁻ ion attack on the chlorine of the CCl₂ group, followed by protonation of the resulting anion. Consequently, the reaction of **2** with MeO⁻ still cannot give the desired geminal Ad_N-E intramolecular EE.

In the reaction of **2** with thiolate ions, we are again confronted with the question of regioselectivity, namely, whether the chlorine replacement product is RSC-(Br)=CCl₂ or RSC(Cl)=C(Br)Cl, and therefore, whether the intramolecular element effect is geminal or vicinal. The measured k_{Br}/k_{Cl} EEs are 0.13 with MeS⁻ and 0.32 with PhCH₂S⁻, i.e., the value is higher for the softer nucleophile. It seems highly unlikely that the intermediate carbanion [Cl₂C-C(Cl)(Br)SR]⁻ would expel Cl⁻ much easier than Br⁻ when both halogens are geminal. Moreover, in contrast with **4**, the AM1 calculations showed that the LUMO of the substrate is almost equally localized on both carbon atoms (44% on CClBr and 47% on CCl₂).²⁰ Finally, the methylthio and benzylthio trihaloethylenes were identical with the monobromo replacement products in the reaction of **1** with MeS⁻ and PhCH₂S⁻, indicating that they have structure **14**. We therefore interpret our reactions as reflecting a competitive attack of the thio nucleophiles on both carbons of **2**. Attack at C_β generates [Cl₂C(SR)C(Br)Cl]⁻ (**16**), from which only Cl⁻ can be expelled, while attack at C_α results in Br⁻ expulsion or Cl⁻ expulsion. Consequently, two element effects are obtained. The ratio of the chlorine replacement to the bromine replacement product reflects the ratio of attack on C_α vs C_β and is therefore the vicinal element effect. The fact that none of Cl₂C=C(Br)SR is formed indicates a high geminal element effect, as was observed in the reactions of **1**. Finally, 1-(benzylthio)-1,2-dichloroethylene is also formed in the reaction with PhCH₂S⁻, most likely by a vinylic substitution of one halogen and a halophilic reaction (followed by protonation) on a different vicinal halogen.

Reactions of 1,2-Dibromo-1,2-dichloroethylene (1). The only compound free from problems of both an elimination-addition process and regioselectivity in the attack of a nucleophile is 1,2-dibromo-1,2-dichloroethylene (**1**), which lacks a vinylic hydrogen and for which C_α = C_β. Consequently, it is suitable for evaluation of an unequivocal geminal element effect. The reactions of **1** with either MeO⁻ or PhCH₂S⁻ were found to be cleaner than those of the other investigated substrates. With MeO⁻ the only product observed is the bromine replacement product MeOC(Cl)=C(Br)Cl (**6**). None of the chlorine replacement product was observed. In the reaction with PhCH₂S⁻, the only monosubstitution product observed was again the benzylthio debromination product NuC(Cl)=C(Br)Cl (**17**, Nu = PhCH₂), and none of the benzylthio dechlorination product was observed. In addition, a single monosubstituted, monohalogen reduction product PhCH₂SC(Cl)=CHCl was obtained and no chlorine was replaced during its formation. Reaction with MeS⁻ also gave only the methylthio debromination product **17**, Nu = MeS, and none of NuC(Br)=C(Br)Cl (**18**, Nu = MeS). These are important observations since they amount to a high k_{Br}/k_{Cl} intramolecular geminal EE with both nucleophiles. Unfortunately, this conclusion

(22) (a) Schneider, H. J.; Bagnell, J. J. *J. Org. Chem.* **1961**, *26*, 1984. (b) Schneider, H. J.; Bagnell, J. J.; Murdoch, G. C. *J. Org. Chem.* **1961**, *26*, 1987.

(23) Helmkamp, G. K.; Olsen, B. A.; Pettitt, D. J. *J. Org. Chem.* **1965**, *30*, 676.

(24) Bodrikov, I. V.; Kovaleva, L. I.; Zefirov, N. S. *Zh. Org. Khim.* **1976**, *12*, 2476.

(25) Trofimov, B. A.; Shainyan, B. A. In: *The Chemistry of Functional Groups. Suppl. S. The Chemistry of Sulfur-Containing Functional Groups*; Patai, S., Rappoport, Z., Eds.; J. Wiley & Sons: Chichester; 1993; pp 659-797.

(26) Krespan, C. G.; McKusick, B. C. *J. Am. Chem. Soc.* **1961**, *83*, 3434. Krespan, C. G. *J. Am. Chem. Soc.* **1961**, *83*, 3438.

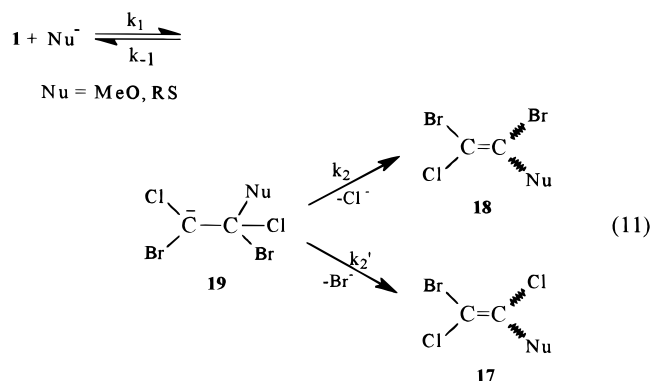
(27) Voronkov, M. G.; Martynov, A. V.; Mirskova, A. N. *Sulfur Rep.* **1986**, *6*, Part 2, 77.

could not be extended to *t*-BuS⁻ ion since it did not give any substitution product. If we assume that 0.1% of the chlorine replacement product could have been detected, as found for several other products obtained in this study, and if we add the reduction/substitution product to the monosubstitution product, then the geminal element effects should be ≥ 107 , ≥ 43 , and ≥ 100 with PhCH₂S⁻, MeS⁻, and MeO⁻, respectively. Since (a) the structures of the products in this system are unambiguous, (b) the values are high, (c) the values are lower limits to the geminal EE, and (d) highly unlikely errors of 100% will still retain high EE values, we conclude that errors, e.g., due to the lack of calibration, are not going to affect our major conclusion that the geminal EEs are high.

If the process investigated is one of the possible variants of the "addition-elimination" type nucleophilic vinylic substitution,^{3,10,19} in which the nucleophile attacks the vinylic carbon and the leaving group is expelled from the formed transition state (TS) or a carbanionic intermediate, two cases can be envisioned.

(a) The reaction is a single step substitution occurring via a single TS where bond formation to the nucleophile and cleavage of the C-halogen bond occur concertedly, i.e., eq 1 with k_1 and k_{-1} merging into a single step process, i.e., **1** is a transition state rather than an intermediate. In this case there are two different single step TSs, chloride ion is expelled in one of them and bromide ion is expelled in the other, and since bromide is a better nucleofuge, the energy of the latter TS is much lower, leading to the observed high geminal element effects. We note that each one of these TSs can have two completely different configurations: (i) the nucleophilic attack can be on the π^* orbital, perpendicular to the double bond, and the process involves formation and cleavage of the bonds as well as intramolecular rotation required to achieve the proper stereoelectronic configuration (antiperiplanar arrangement of the leaving group-carbon bond and the carbanionic lone pair) in order to obtain the substitution product; (ii) an in-plane S_N2 nucleophilic substitution where the nucleophile attacks from the back of the leaving group.

(b) The reaction proceeds by the customary two-step nucleophilic vinylic substitution (eq 11).^{3,10}



In this case, the expulsion of the leaving group(s) takes place starting from a discrete intermediate carbanion. Two mechanistic probes to distinguish some of these alternatives are the stereochemistry of the reaction and the "external" EE. The in-plane reaction should lead to inversion, whereas the perpendicular attack either via a single-step or a multistep route should lead to retention. Unfortunately, we could not separate the *E* and *Z* isomers of **1**, and we do not know if they are stable to isomeriza-

tion (e.g., *E*- and *Z*-BrC(F)=C(Br)F are unstable to mutual isomerization²⁾, although both isomers could be detected by ¹³C NMR. Consequently, the stereochemical tool could not be applied and the remaining tools are the intramolecular and intermolecular EEs. The ratio of the bromine-replaced to the chlorine-replaced products in eq 11 (i.e., the geminal EE) is equal to the rate ratio for expulsion of Br⁻ vs Cl⁻ from the same "ground state" carbanion NuC(Br)(Cl)C(Br)Cl⁻ (**19**).¹¹ As expulsion of different leaving groups occurs from different conformations of carbanion **19**, characterized by antiperiplanar arrangement of the carbanionic lone pair and the leaving group expelled, there must be a bifurcation point on the potential energy surface preceding to and resulting in two different TSs. The EE in this case is a measure of how early or late the corresponding TSs are. Judging from intermolecular element effects in S_N1 reactions, i.e., $k_{\text{ion}}(\text{RBr})/k_{\text{ion}}(\text{RCl})$, the ratios²⁸ are mostly between 1 and 2 orders of magnitude in an endothermic carbocation forming C-X bond cleavage, and a much lower value is anticipated for an expected exothermic reaction in which a β -halo carbanion is converted to a halide ion and a neutral alkene. The TS in the latter reaction should be much earlier than in an S_N1 reaction and the element effect is therefore expected to be lower. Note, however, that an S_N1, E1, or even E2 reaction differs somewhat from what we have in our case, since in our case the nonexpelled halogen stabilizes the TS, so we are comparing expulsion of Cl⁻ in a Br-stabilized TS to an expulsion of Br⁻ in a Cl-stabilized TS. Unfortunately, we have no data for a proper comparison for the product ratio derived from loss of bromide and chloride ion, i.e., on S_N1 reactions of RR'C(Br)Cl solvolysis and on E1 or E2 reactions of RR'CH-CR''(Br)Cl, respectively. Nevertheless, since the polar and resonance effects of Cl and Br are similar, this effect could be neglected in the first approximation. If so, an independent assessment of the intramolecular EE values can be made based on the known data for energy of Br⁻ vs Cl⁻ formation in ionization processes, hydration, and transfer from water to various solvents. The heterolytic bond dissociation energies for RX → R⁺ + X⁻ in the gas phase for R = Me, Et, *n*-Pr, *i*-Pr, *t*-Bu, Ph, vinyl, allyl, and PhCH₂ are by 6–9 kcal mol⁻¹, averaging 7.7 kcal mol⁻¹, higher for X = Cl than for X = Br.²⁹ For hydration, i.e., transfer from the gas phase to water, $\Delta G_{\text{hyd}}^0 = -81.3$ (Cl⁻) and -75.3 (Br⁻) kcal mol⁻¹ and $\Delta H_{\text{hyd}}^0 = -87.2$ (Cl⁻) and -80.1 (Br⁻) kcal mol⁻¹. The maximum predicted EE in terms of ΔH is therefore 0.7 kcal mol⁻¹, i.e., less than 1 order of magnitude. For transfer of X⁻ from water to MeCN, $\Delta G_{\text{trans}} = 10.1$ (Cl⁻), 7.4 (Br⁻) kcal mol⁻¹ and $\Delta H_{\text{trans}} = 4.5$ (Cl⁻), 1.7 (Br⁻) kcal mol⁻¹; for transfer from water to DMSO, $\Delta G_{\text{trans}} = 9.8$ (Cl⁻), 6.5 (Br⁻) kcal mol⁻¹ and $\Delta H_{\text{trans}} = 4.8$ (Cl⁻), 1.2 (Br⁻) kcal mol⁻¹.³⁰ Hence, $\Delta\Delta G_{\text{trans}}$ (Cl⁻ - Br⁻) = 2.7 (MeCN), 3.3 (DMSO) kcal mol⁻¹ and $\Delta\Delta H_{\text{trans}}$ (Cl⁻ - Br⁻) = 2.8 (MeCN), 3.6 (DMSO) kcal

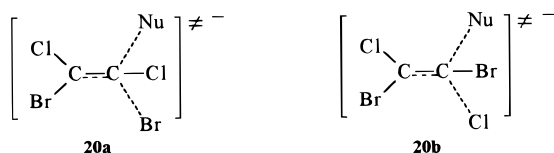
(28) For few collections of several $k_{\text{Br}}/k_{\text{Cl}}$ ratios, see: Streitwieser, A., Jr. *Solvolytic Displacement Reactions*; McGraw-Hill: New York, 1962; p 30 and ref 40 therein; Rappoport, Z.; Gal, A. *J. Chem. Soc., Perkin Trans. 2* **1973**, 301. For several other values, see: Ross, S. D.; Labes, M. M. *J. Am. Chem. Soc.* **1957**, 79, 4155. Gelles, E.; Hughes, E. D.; Ingold, C. K. *J. Chem. Soc.* **1954**, 2918; Pocker, Y. *J. Chem. Soc.* **1960**, 1972. Heinonen, K.; Tomilla, E. *Suom. Kemistil.* **1965**, 38B, 9.

(29) Morrison, R. T.; Boyd, R. N. *Organic Chemistry*, 6th ed.; Prentice Hall: New York, 1992; p 22.

(30) Marcus, Y. In *Liquid-Liquid Interfaces. Theory and Methodology*; Volkov, A. G., Deamer, D. W., Eds.; CRC Press: Boca Raton, 1996; Chapter 3, p 321.

mol^{-1} . Consequently, the maximum EE (in kcal mol^{-1}) is 3.5 (in $\Delta\Delta\text{H}$) or 4.5 (in $\Delta\Delta\text{G}$) in MeCN and 5.3 ($\Delta\Delta\text{G}$) or 4.0 ($\Delta\Delta\text{H}$) in DMSO. At room temperature the maximum $k_{\text{Br}}/k_{\text{Cl}}$ EE will be two to three orders of magnitude. This is consistent with the observed values for $\text{S}_{\text{N}}1$, E1 and E2 reactions which are mostly <100 .²⁸ Our intramolecular EE can therefore be regarded as high for expulsion of halide ions from a carbanion and pathway a seems a reasonable alternative.

If we accept the high intramolecular EE as reflecting a concerted transition state for the substitution, cf. **20**, this must be necessarily reflected also in a high intermolecular EE.



For this reason, the relative reaction rates of **1** and tetrachloroethylene were compared in Tables 7 and 8. Despite the relatively large error, the obtained intermolecular EEs of 9.1 ± 1.7 with MeO^- and 11.2 ± 2.7 with PhCH_2S^- are significantly higher than any of the intermolecular $k_{\text{Br}}/k_{\text{Cl}}$ EEs obtained previously in vinylic substitution.¹⁰ Hence, according to current thinking, these values corroborate the deduction that a C–X bond cleavage is part of the rate-determining step in the substitution. Whereas this is an unusual conclusion, we note that if a single step substitution will be found at all, it is likely to be found in systems such as **1**, where the substituents are not capable of extensive stabilization of the negative charge formed in the transition state. Additional studies, preferably with structurally related systems, using the EEs and other probes will be valuable for strengthening our conclusion.

Judging from the assignment made above and the results of Table 1, the *E* isomer of **1** is more reactive than the *Z* isomer. Analysis of the energies and localization of MOs of *E*-**1** and *Z*-**1** revealed²⁰ that the two lowest unoccupied MOs of **1** are nearly similarly localized. The LUMOs are $>90\%$ localized on the carbon atoms and they are of virtually the same energy (-0.644 eV). The next vacant orbital is 40% localized on the carbons and 60% on the halogens. For the *Z* isomer it is 20% localized on chlorines and 40% on bromines, while for the *E* isomer it is $>56\%$ localized on bromines and only 4% on chlorines. Its energy for the *E* isomer lies 3.4 kcal mol^{-1} lower than for the *Z* isomer. This can explain a higher reactivity of the *E* isomer.

The trisubstituted alkenes $\text{RSC}(\text{Cl})=\text{CHCl}$ formed in the reaction with RS^- seem to arise from protonation of a trisubstituted vinyl anion, which is most likely formed by a bromophilic reaction on either **1** or its monothio substitution product. Such a process is well-known for both simple and functionalized vinyl halides,^{2,6,7,31–33} as also shown above. As shown by one of us, the *Z*- $\text{BrCH}=\text{C}(\text{F})\text{Br}$ is more reactive toward RS^- and leads mainly to the vinylic monosubstitution products $\text{RSC}(\text{F})=\text{CHBr}$, while the less reactive *E* isomer gives predominantly the product $\text{RSC}(\text{F})=\text{CH}_2$ of halophilic reduction.³³

Experimental Section

Melting points were determined with a Thomas-Hoover instrument and are uncorrected. GC analysis was performed on a LKhM-80 chromatograph, using 3×2000 mm columns of 5% silicon elastomer SE-30 on Chromaton N-AW HMDS, a catharometer detector, and helium as carrier gas, or on a Packard-436 chromatograph, with FID and FPD detectors. GC-MS analysis was performed on LKB 2091 and Finnigan ITS-40 instruments at 70 eV on a 60 m capillary column with SE-30 in a programming mode (injector temperature 250°C , initial temperature 100°C , increase at a rate of $16\text{--}20^\circ/\text{min}$ for ca. 10 min, and a few minutes at the final temperature). HPLC experiments were conducted with a Merck-Hitachi L-6200 instrument with a UV detector. Mass spectra were obtained on a MAT 311 mass spectrometer, UV spectra with a UVIKON-930 Contron spectrophotometer, and IR spectra with Perkin-Elmer 157G and 1600-FT-IR instruments. ^1H and ^{13}C NMR spectra were recorded on Bruker WP-200 (200 MHz for ^1H , 50.3 MHz for ^{13}C), Bruker AMX-400 (400 MHz for ^1H , 100.6 MHz for ^{13}C), and Varian VXR 500 (500 MHz for ^1H , 125.7 MHz for ^{13}C) instruments, in CDCl_3 .

Solvents and Materials. Ether (Frutarom) was dried over sodium metal overnight before use. Methanol (99%) was dried with magnesium metal. All other solvents and reagents were commercially available and were used without further purification.

Synthesis of the Polyhaloethylenes. 1,2-Dibromo-1,2-dichloroethylene (1). (1) Compound **1** was prepared from *trans*-1,2-dichloroethylene by a sequence of two consecutive brominations with Br_2 /dehydrobrominations (with liquid ammonia) according to the method of Mkryan.³⁴ This method was applied after finding that van der Walle's method,³⁵ which involves two consecutive brominations (with Br_2)/dehydrobrominations (first with PhNH_2 , then with KOH/EtOH), failed due to difficulties both in removing the excess aniline and in the dehydrobromination with KOH . These difficulties disappeared when Et_3N was used instead of aniline: To 1,1,2-tribromo-1,2-dichloroethane (3 g) prepared by the above sequence from dichloroethylene was added triethylamine (1.2 mL) in acetonitrile (10 mL), and the reaction mixture was kept for 22 h at room temperature and then washed with water, dried (MgSO_4), and distilled under vacuo. The fraction boiling at $88^\circ\text{C}/18$ mmHg (0.8 g, 35%) was collected and identified as an 4:3 *E/Z* mixture of **1**. For details and spectra see the Results section. The yield was improved when piperidine was used for the dehydrobromination instead of liquid ammonia, as described below for preparation of compound **2**.

(2) Compound **1** was also prepared according to the method of Pielichowski¹⁴ from dichloroacetylene which, in turn, was obtained from trichloroethylene and aqueous NaOH solution with a catalytic amount of benzyltriethylammonium chloride. The formed ether complex of dichloroacetylene was brominated by 1 equiv of Br_2 in CCl_4 .

1-Bromo-1,1,2-trichloroethylene (2). Into trichloroethylene (100 mL, 1.1 mol) was added bromine (60 mL, 1.15 mol) dropwise with stirring and irradiation with a sun lamp. The mixture was washed after 24 h with 10% aqueous $\text{Na}_2\text{S}_2\text{O}_3$ solution, dried (MgSO_4), and distilled, affording 1,2-dibromo-1,1,2-trichloroethane (257 g, 75%), bp $92\text{--}6^\circ\text{C}/18$ mmHg. To a solution of the dibromotrichloroethane (137 g, 0.46 mol) in dry ether (100 mL) was added piperidine (45 mL, 0.46 mol) with stirring. After 24 h the precipitated piperidine hydrobromide was filtered off and washed with dry ether and the combined filtrate was distilled at $53\text{--}4^\circ\text{C}/18$ mmHg, giving 1-bromo-1,1,2-trichloroethylene (81 g, 82%), which was pure according to the ^1H and ^{13}C NMR spectra. Attempts to prepare the compound according to Mkryan's method³⁴ using liquid ammonia gave a mixture of the desired **2** and dibromotrichloroethane which could not be separated efficiently by distillation.

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1-Bromo-1-chloro-2-methylpropene (3) was prepared according to Cunico and Han's procedure.¹⁵

1,2-Dichloro-1-bromoethylene (4) was obtained by addition of bromine to (*E*)-1,2-dichloroethylene followed by debromination of the mixture of diastereomers of 1,2-dichloro-1,2-dibromoethane (two singlets in a 1:1 ratio at δ 6.00 and 6.05 in the ¹H, and at δ 61.30 and 61.49 in the ¹³C NMR spectra) with piperidine in ether. The fraction boiling at 45–50 °C/30 mmHg was collected.

1,2-Dibromo-1-chloroethylene (5) was prepared according to a procedure similar to that used for preparation of **1**.¹⁴ Chloroacetylene was obtained as its ether complex by reaction of an *E/Z* mixture of 1,2-dichloroethylene in ether with an aqueous NaOH solution and a catalytic amount of benzyltriethylammonium chloride. The ether complex which was evolved as a gas from the solution was passed into the ethereal solution of 1 equiv of bromine. Fractional distillation gave a 75% yield (fraction boiling at 50–55 °C/30 mmHg was collected) of **5** as a 2:1 *E/Z* mixture.

Reactions with MeONa. The reactions of chlorobromoethylenes **1**, **2**, **4**, and **5** with an equimolar amount of dry MeONa were conducted in MeCN at 80 °C and in DMF at 100 °C in the course of 30–60 min. Sodium methoxide was prepared by dissolution of sodium metal in dry methanol, evaporation of the solvent, and drying under high vacuo. Since the conversion to products under these conditions was low, individual products were not isolated. Instead, the reaction mixtures in MeCN or DMF were poured into water and extracted with chloroform, and the organic phase was analyzed by GC, GC–MS, and ¹H and ¹³C NMR spectroscopy.

Reactions with RSNa. Bromochloroethylenes **1**, **2**, **4**, and **5** in ca. 8-fold molar excess were reacted with sodium thiolates RSNa (R = PhCH₂, Me, *t*-Bu) in MeCN at room temperature under nitrogen for 24 h in order to ensure nearly exclusive formation of the monosubstitution products. Unfortunately, separation of the latter by chromatography (silica columns, preparative OV-101 column, analytical GC or HPLC PR and cyanide columns) failed. Therefore, the analysis was mainly conducted by GC–MS and the relative intensities given are

based on the measured intensities of the signals without calibration; the structural assignment was made by MS. In addition, ¹H and ¹³C NMR spectroscopies were used in appropriate cases, and the single products from tetrachloro- and trichloroethylenes that can give only the chlorine substitution products were isolated.

Reactions with 3. The reaction of an 8-fold excess of **3** with MeS[−]Na⁺ in acetonitrile was conducted under nitrogen for 15–144 h at room temperature or for 18 h at 80 °C. No reaction took place according to NMR or GC–MS analysis. When the reaction between **3** and PhCH₂S[−]Na⁺ was conducted for 23 h at 80 °C, no substitution product was identified. Dibenzyl disulfide (6.3%) and an unidentified product (5.4%) whose higher *m/z* value is at 253 and which contains a benzyl moiety and does not contain Br and Cl was formed. Apparently, **3** is inert to substitution under the reaction conditions.

Measurement of External EE. Compound **1** and tetrachloroethylene (5 mmol each) were dissolved in 1.5–2 mL of MeCN, and 10 mmol of dry MeONa or PhCH₂SNa was added under an argon atmosphere. In the case of PhCH₂SNa, the reaction was self-heated. GC measurements were started immediately (1–2 min after mixing), and the reactions were followed until there was virtually no more changes in the ratio of the substrates. The values of the external EE were calculated from eq 6.

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