Bromochlorination of Alkenes with Dichlorobromate (1−) Ion. IV.[1,2] Regiochemistry of Bromochlorinations of Alkenes with Molecular Bromine Chloride and Dichlorobromate (1−) Ion

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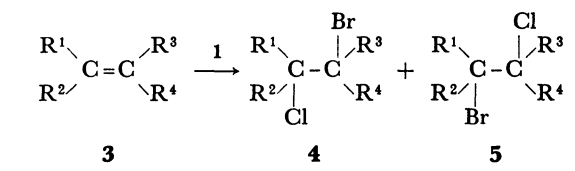
The regioselectivity of the addition of molecular bromine chloride to alkenes is dependent on both the steric and electronic effects of the alkyl substituent. In contrast, the regioselectivity of the addition of dichlorobromate (1−) ion to alkenes is controlled mainly by the steric effect of the substituent.

The regioselectivity of bromochlorination of phenyl- and vinyl-substituted alkenes has been shown to be markedly dependent both on the bromochlorinating agent and on the structure of alkene employed.[1-3] There have been a few investigations on the regiochemistry of bromochlorination of alkyl-substituted ethylenes with molecular bromine chloride and dichlorobromate(1−) ion, and the addition of BrCl to such alkenes as propene, 3-chloro-1-propene, and 1-hexene has been reported to give both Markownikoff and *anti*- Markownikoff adducts.[2,5] We have also reported that dichlorobromate(1−) ion reacted with propene and 3-chloro-1-propene to give two regioisomers.[1] However, no systematic study has been carried out on the bromochlorination reaction of alkyl-substituted ethylenes. As a continuation of our studies[1-3] we have carried out a study on the regiochemical effect of the alkyl substituent in the addition of molecular bromine chloride and dichlorobromate (1−) ion to various alkenes.

Results and Discussion

Reactions of a series of alkenes **3a-l** with tetrabutylammonium dichlorobromate(1−) (**1**) in dichloromethane gave the corresponding bromo chloro compounds **4a—l** and **5a—l** in good yields (Table 1 and Scheme 1). Similar reactions of methylenecycloalkanes **3m—n** with **1** also gave the corresponding bromo chloro compounds **4m—n** and **5m—n** in good yields (Table 1 and Scheme 2).

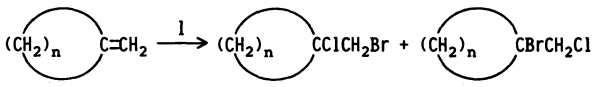
The orientation of halogen atoms in all the addition products was elucidated mainly on the basis of chemical shifts of the carbon bearing bromine and chlorine atoms in ^{13}C NMR spectra, since it has been observed that the carbon atom bearing a chlorine atom is deshielded relative to the one bearing a bromine atom.[6] Meanwhile, the structures of two regioisomers **4** and **5** have been determined by comparison of their ^{13}C NMR spectra with those of the corresponding



3 **4** **5**

	R^1	R^2	R^3	R^4		R^1	R^2	R^3	R^4
a	Et	H	H	H	**g**	Et	H	Me	H
b	*n*-Pr	H	H	H	**h**	Me	Me	H	H
c	*n*-Bu	H	H	H	**i**	Et	Et	H	H
d	*i*-Pr	H	H	H	**j**	Me	Me	Me	H
e	*t*-Bu	H	H	H	**k**	Et	Me	H	Me
f	Et	H	H	Me	**l**	Et	Me	Me	H

Scheme 1.



$n=4$: **3m** **4m** **5m**
$n=5$: **3n** **4n** **5n**

Scheme 2.

Table 1. Bromochlorination of Alkenes with **1** in CH_2Cl_2[a]

Alkenes	Product composition/%[b]		Yield/%[c]	Alkenes	Product composition/%[b]		Yield/%[c]
3	**4**	**5**		**3**	**4**	**5**	
3a	44	56	80	**3h**	69 (66)	31 (34)	78
3b	43	57	82	**3i**	67 (68)	33 (32)	76
3c	41	59	83	**3j**	71	29	79
3d	24	76	78	**3k**	68[f]	32[f]	81
3e	0	100	74	**3l**	47[g]	53[g]	80
3f	40[d]	60[d]	82	**3m**	92 (89)	8 (11)	75
3g	33[e]	67[e]	81	**3n**	26 (25)	74 (75)	79

a) Reactions were carried out with 30 mmol of **1**, 36 mmol of alkene, and 50 ml of CH_2Cl_2 at 0 °C. b) Percentages are normalized to 100%. Determined by ^{13}C NMR analysis. The figures in parentheses represent product distributions determined by ^1H NMR analysis. c) Isolated yield based on **1**. d) *erythro*. e) *threo*. f) (*RS,SR*). g) (*RS,RS*).

Table 2. Bromochlorination of Alkenes with **2** in CH_2Cl_2[a]

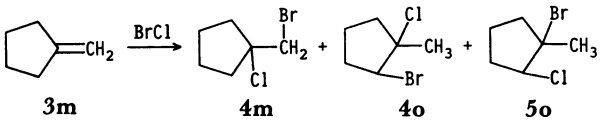
Alkenes	Product composition/%[b]		Yield/%[c]	Alkenes	Product composition/%[b]		Yield/%[c]
3	**4**	**5**		**3**	**4**	**5**	
3a	58	42	61	**3h**	86	14	72
3b	55	45	72	**3i**	87	13	70
3c	58	42	65	**3j**	86	14	71
3d	41	59	69	**3k**	84[f]	16[f]	70
3e	11	89	68	**3l**	68[g]	32[g]	69
3f	48[d]	52[d]	72	**3m**	100	0	11
3g	36[e]	64[e]	69	**3n**	82	18	55

a) Reactions were carried out with 10 mmol of **2**, 12 mmol of alkene, and 50 ml of CH_2Cl_2 at 0 °C. b) Percentages are normalized to 100%. Determined by ^{13}C NMR analysis. c) Determined by GLC analysis. d) *erythro*. e) *threo*. f) (*RS,SR*). g) (*RS,RS*).

dibromo and dichloro compounds. Control experiments revealed that all the bromo chloro compounds are stable under the reaction conditions.

Treatments of a series of alkenes **3a—l** with molecular bromine chloride (**2**) in CH_2Cl_2 also gave the corresponding bromo chloro compounds **4a—l** and **5a—l** (Table 2). The yields are lower than those in the reaction with **1** due to formation of dibromo- and dichloroalkanes. The formation of these by-products in the reaction is undoubtedly due to the attack of both Br_2 and Cl_2, which are formed from and in equilibrium with **2**, on alkenes.[7]

On the other hand, the reaction of methylenecyclopentane (**3m**) with **2** gave a mixture of 2-bromo-1-chloro- and 1-bromo-2-chloro-1-methylcyclopentanes (**4o** and **5o**, 54.5% yield by GLC analysis) as the major products. The expected bromo chloro compound **4m** (11.0% yield by GLC analysis) was a minor component (Scheme 3 and Table 2). The formation of



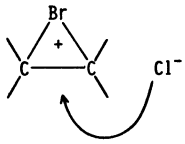
3m **4m** **4o** **5o**

Scheme 3.

both **4o** and **5o** may be due to the competing allylic halogenation which produces hydrogen halide. The hydrogen halide thus formed is considered to isomerize the terminal alkene **3m** into a more stable internal alkene **3o** (1-methylcyclopentene), to which **2** is then presumed to add. In fact, the presence of **3o** was confirmed by ^1H NMR analysis of the reaction mixture. Furthermore, the ratio of the two regioisomers (**4o**:**5o**=86:14) is the same as that observed for the reaction of **3o** with **2**. A similar reaction has been reported for the addition of bromine to **3m**.[8] Similarly, the reaction of methylenecyclohexane (**3n**) also gave a small amount of 2-bromo-1-chloro- and 1-bromo-2-chloro-1-methylcyclohexane (**4p** and **5p**).

An inspection of the data in Tables 1 and 2 clearly reveals that the regiochemistry of the addition of **1** to alkenes is strikingly different from that of the reaction of **2**. Therefore, the product-determining step must be different in these two reactions.

Regioselectivity of the Reaction of 3 with 2. The reaction with **2** can best be explained by the AdE_{C_1}-type mechanism involving the attack of chloride ion to a bridged bromonium ion intermediate **6**:[5,9] a similar intermediate has also been suggested for the bromination of alkenes with molecular bromine.[10]



(6)

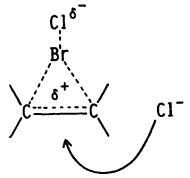
As shown in Table 2, the bromochlorination of the unsymmetrical alkenes, 1,2-dialkyl- **3f** and **3g** and 1,1,2-trialkylethylenes **3k** and **3l**, with **2** gave completely *anti* stereospecific adducts. This supports further the assumption that the intermediate in the bromochlorination of alkyl-substituted ethylenes with **2** resembles the bridged ion **6**. These results are in marked contrast to the stereoselective addition of **2** to phenyl- or vinyl-substituted alkenes, which involves a very weakly bridged ion intermediate.[2,3] Thus, the *anti* stereospecific addition of **2** to **3k** and **3l** would rule out the possibility of carbonium ion-like intermediate which is considered to be involved in the bromination of these alkenes with bromine.[10]

Both the steric and the electronic effect of the alkyl substituent on ethylene linkage would play a major role in the orientation of the approach of chloride ion on the bromonium ion intermediate **6**. As shown in Table 2, nearly the same ratio of regioisomers is given for the reactions of 1-butene (**3a**), 1-pentene (**3b**), and 1-hexene (**3c**) with **2**, which indicates the effects of linear alkyl substituents to be nearly the same. Meanwhile, the replacement of the hydrogen on ethylene by isopropyl (**3d**) or *t*-butyl (**3e**) results in the formation of an increasing amount of the *anti*-Markownikoff adduct **5d** or **5e**. This reveals clearly that the addition of **2** can be influenced by steric factors of the bulky groups.

On the other hand, the additions of **2** to 1,1-disubstituted **3h** and **3i** and 1,1,2-trisubstituted ethylenes **3j**, **3k**, and **3l** or methylenecycloalkanes **3m** and **3n** gave regioselective Markownikoff adducts **4** (Table 2).

These results imply that the attack of chloride ion on the bromonium ion intermediate **6** occurs at the more substituted carbon atom. Thus, the orientation of bromochlorination with **2** would be due to the electronic effect of the 1,1-dialkyl substituent which stabilizes the developed cationic character on the more substituted carbon atom in the intermediate **6**. A similar accumulative electronic effect of dialkyl substituent groups on the regiochemistry has previously been observed in the bromination of these alkenes in methanol.[11]

Regioselectivity of the Reaction of 3 with 1. We have previously suggested that the reaction of alkenes with **1** can be best explained by the $AdEC_2$-type mechanism involving the attack of chloride ion on the three-centered π-complex intermediate **7** with a very little charge development on the unsaturated carbon.[2,3]



(7)

Therefore, there would be a relatively small demand for electronic stabilization of the reaction center by alkyl substituents on the intermediate **7**. As expected, the amount of the *anti*-Markownikoff adduct **5** in the addition with **1** (Table 1) is generally larger than that in the addition with **2** (Table 2). Thus, the addition of **1** to linear alkyl-substituted ethylenes **3a**, **3b**, and **3c** was found to be slightly more regioselective in an *anti*-Markownikoff manner than that in the addition of **2**. Meanwhile, the replacement of the hydrogen on ethylene by an isopropyl (**3d**) or a *t*-butyl group (**3e**) results in the formation of a larger amount of the *anti*-Markownikoff adduct **5** than that in the addition of **2**. It is interesting to note that only the *anti*-Markownikoff adduct **5e** is obtained in the reaction of 3,3-dimethyl-1-butene (**3e**), as anticipated from the greater steric requirement of *t*-butyl group. The reaction of methylenecyclohexane (**3n**) with **1** also gives a regioselective *anti*-Markownikoff adduct **5n**, where the opposite orientation results from that of the reaction with **2**. All these results support that the steric effect outweighs the electronic effect of the alkyl substituent in the reaction with **1**.

However, the reaction of **1** to 1,1-dialkyl- **3h** and **3i** and 1,1,2-trialkylethylenes **3j** and **3k** or methylenecyclopentane (**3m**) gave the regioselective Markownikoff adduct **4** (Table 1). As in the reaction with **2**, the electronic effect of the 1,1-dialkyl groups would overcome partially the steric influence.

Experimental

NMR spectra were recorded on a JEOL JNM FX-60Q and a JEOL C-60HL spectrometer using TMS as the internal standard. Mass spectra were recorded on a JMS-D-300 mass spectrometer. GLC analyses were performed on a Yanako G-180 gas chromatograph with a Silicone SE-30 (5%)-Chromosorb WAW DMCS (2 m) column with helium as the carrier gas. Tetrabutylammonium dichlorobromate(1−) (**1**) was prepared by the known procedure.[12] All the organic starting materials, including the solvents, were distilled before use. Bromine chloride (**2**) was prepared by adding an equimolar amount of bromine to chlorine–carbon tetrachloride solution. 1,2-Dibromoalkanes **8a—n** were prepared by bromination of alkenes **3a—n** with bromine, respectively. 1,2-Dichloroalkanes **9a—n** were prepared by chlorination of alkenes **3a—n** with chlorine, respectively.

Reaction of Alkenes 3a—n with 1. Details of the reaction have previously been reported.[1,2] To a solution of **3** (36 mmol) in CH_2Cl_2 (50 ml) was added **1** (11.8 g, 30 mmol) at 0°C over 20 min with stirring. After the usual work-up, the products were purified by distillation. Although attempts to separate **4** and **5** were unsuccessful, these structures were determined by comparison of their ^{13}C NMR spectra with those of the corresponding dibromo and dichloro analogs.

A Mixture of 1-Bromo-2-chloro- and 2-Bromo-1-chlorobutanes (4a and 5a) from 1-Butene (3a): Bp 82°C/110 mmHg (1 mmHg=133.322 Pa); MS M^+ *m/z* (rel intensity) 170, 172, and 174 (100:135:32); ^1H NMR ($CDCl_3$) δ=1.04 (3H, t, J=6.5 Hz), 1.40—2.30 (2H, m), and 3.50—4.30 (3H, m); ^{13}C NMR ($CDCl_3$) (the asterisk indicates **5a**) δ=10.1, 11.1,* 28.4,* 28.8, 35.8, 47.6,* 54.9,* and 62.1. Although attempts to separate **4a** and **5a** were unsuccessful, these assignments were supported for dibromo and dichloro analogs as follows: 1,2-dibromobutane (**8a**), ^{13}C NMR ($CDCl_3$) δ= 11.0, 29.0, 35.6, and 54.3; 1,2-dichlorobutane (**9a**), ^{13}C NMR ($CDCl_3$) δ=10.2, 28.2, 47.8, and 62.6.

A Mixture of 1-Bromo-2-chloro- and 2-Bromo-1-chloropentanes (4b and 5b) from 1-Pentene (3b): Bp 70—72°C/ 50 mmHg; MS M^+ *m/z* (rel intensity) 184, 186, and 188 (100:134:36); ^1H NMR ($CDCl_3$) δ=0.83—2.30 (7H, m) and 3.33—4.35 (3H, m); ^{13}C NMR ($CDCl_3$) (the asterisk indicates **5b**) δ=13.3,* 13.4, 19.2, 20.2,* 36.5, 37.4,* 37.8, 48.3,* 53.2,* and 60.6. These assignments were supported for dibromo and dichloro analogs as follows: 1,2-dibromopentane (**8b**), ^{13}C NMR ($CDCl_3$) δ=13.3, 20.1, 36.3, 38.0, and 52.7; 1,2-dichloropentane (**9b**), ^{13}C NMR ($CDCl_3$) δ=13.5, 19.2, 37.1, 48.3, and 60.9.

A Mixture of 1-Bromo-2-chloro- and 2-Bromo-1-chlorohexanes (4c and 5c) from 1-Hexene (3c): Bp 95—96°C/ 50 mmHg; MS M^+ *m/z* (rel intensity) 198, 200, and 202 (100:129:31); ^1H NMR ($CDCl_3$) δ=0.93—2.40 (9H, m) and 3.50—4.30 (3H, m); ^{13}C NMR ($CDCl_3$) (the asterisk indicates **5c**) δ=13.9, 22.0,* 22.1, 28.0, 28.9,* 35.1,* 35.5, 36.5, 48.2,* 53.5,* and 60.8. These assignments were supported for dibromo and dichloro analogs as follows: 1,2-dibromohexane (**8c**), ^{13}C NMR ($CDCl_3$) δ=13.9, 21.9, 28.8, 35.7, 36.3, and 53.0; 1,2-dichlorohexane (**9c**), ^{13}C NMR ($CDCl_3$) δ= 13.9, 22.1, 27.9, 34.7, 48.2, and 61.2.

A Mixture of 1-Bromo-2-chloro- and 2-Bromo-1-chloro-3-methylbutanes (4d and 5d) from 3-Methyl-1-butene (3d): Bp 68—70°C/50 mmHg; MS M^+ *m/z* (rel intensity) 184, 186, and 188 (100:130:35); ^1H NMR ($CDCl_3$) δ=0.99 (6H, t, J=6.6 Hz), 2.00—2.57 (1H, m), and 3.63—4.33 (3H, m); ^{13}C NMR ($CDCl_3$) (the asterisk indicates **5d**) δ=15.1, 16.1,* 20.4, 21.4,* 29.6,* 30.8, 34.4, 46.1,* 61.8,* and 67.2. These assignments were supported for dibromo and dichloro analogs as follows:

1,2-dibromo-3-methylbutane (**8d**), ^{13}C NMR ($CDCl_3$) δ=15.5, 21.7, 29.9, 34.1, and 61.5; 1,2-dichloro-3-methylbutane (**9d**), ^{13}C NMR ($CDCl_3$) δ=15.6, 20.2, 30.3, 46.3, and 67.6.

2-Bromo-1-chloro-3,3-dimethylbutane (5e) from 3,3-Dimethyl-1-butene (3e): Bp 95—100°C/50 mmHg; MS M$^+$ *m/z* (rel intensity) 198, 200, and 202 (100:129:31); ^{1}H NMR ($CDCl_3$) δ=1.12 (9H, s) and 3.52—4.13 (3H, m); ^{13}C NMR ($CDCl_3$) δ=27.6, 36.3, 47.6, and 68.8. ^{13}C NMR spectra for dibromo and dichloro analogs are as follows: 1,2-dibromo-3,3-dimethylbutane (**8e**), ^{13}C NMR ($CDCl_3$) δ=27.6, 35.8, 37.0, and 69.0; 1,2-dichloro-3,3-dimethylbutane (**9e**), ^{13}C NMR ($CDCl_3$) δ=26.7, 36.2, 47.1, and 73.7.

A Mixture of *erythro*-2-Bromo-3-chloro- and 3-Bromo-2-chloropentanes (4f and 5f) from *trans*-2-Pentene (3f): Bp 71—72°C/50 mmHg; MS M$^+$ *m/z* (rel intensity) 184, 186, and 188 (100:128:32); ^{1}H NMR ($CDCl_3$) δ=1.07 (3H, t, J=6.8 Hz), 1.33—2.26 (5H, m), and 3.78—4.40 (2H, m); ^{13}C NMR ($CDCl_3$) (the asterisk indicates **5f**) δ=10.5, 11.6,* 23.4, 23.5,* 29.1,* 29.4, 51.8, 59.7,* 63.0,* and 69.0. These assignments were supported for dibromo and dichloro analogs as follows: *erythro*-2,3-dibromopentane (**8f**), ^{13}C NMR ($CDCl_3$) δ=11.4, 25.2, 30.5, 51.8, and 63.2; *erythro*-2,3-dichloropentane (**9f**), ^{13}C NMR ($CDCl_3$) δ=10.4, 22.2, 28.3, 59.5, and 68.6.

A Mixture of *threo*-2-Bromo-3-chloro- and 3-Bromo-2-chloropentanes (4g and 5g) from *cis*-2-Pentene (3g): Bp 72—73°C/50 mmHg; MS M$^+$ *m/z* (rel intensity) 184, 186, and 188 (100:132:35); ^{1}H NMR ($CDCl_3$) δ=1.07 (3H, t, J=6.9 Hz), 1.34—2.24 (5H, m), and 3.77—4.57 (2H, m); ^{13}C NMR ($CDCl_3$) (the asterisk indicates **5g**) δ=11.5, 12.6,* 21.3,* 21.5, 27.3,* 27.7, 52.2, 59.9,* 62.1,* and 68.2. These assignments were supported for dibromo and dichloro analogs as follows: *threo*-2,3-dibromopentane (**8g**), ^{13}C NMR ($CDCl_3$) δ=12.7, 21.6, 27.5, 52.2, and 62.1; *threo*-2,3-dichloropentane (**9g**), ^{13}C NMR ($CDCl_3$) δ=11.4, 20.8, 27.1, 59.7, and 67.9.

A Mixture of 1-Bromo-2-chloro- and 2-Bromo-1-chloro-2-methylpropanes (4h and 5h) from 2-Methylpropene (3h): Bp 79—82°C/90 mmHg; MS M$^+$ *m/z* (rel intensity) 170, 172, and 174 (100:132:34); ^{1}H NMR ($CDCl_3$) (the asterisk indicates **5h**) δ=1.69, 1.83* (6H, 2s), 3.63, and 3.83* (2H, 2s); ^{13}C NMR ($CDCl_3$) (the asterisk indicates **5h**) δ=30.4, 31.0,* 43.7, 55.3,* 62.3,* and 67.1. These assignments were supported for dibromo and dichloro analogs as follows: 1,2-dibromo-2-methylpropane (**8h**), ^{13}C NMR ($CDCl_3$) δ=31.9, 44.7, and 62.1; 1,2-dichloro-2-methylpropane (**9h**), ^{13}C NMR ($CDCl_3$) δ=29.6, 54.6, and 67.6.

A Mixture of 1-Bromo-2-chloro- and 2-Bromo-1-chloro-2-ethylbutanes (4i and 5i) from 2-Ethyl-1-butene (3i): Bp 65—66°C/19 mmHg; MS M$^+$ *m/z* (rel intensity) 198, 200, and 202 (100:130:35); ^{1}H NMR ($CDCl_3$) (the asterisk indicates **5i**) δ=0.90—1.14 (6H, m), 1.66—2.11 (4H, m), 3.63, and 3.87* (2H, 2s); ^{13}C NMR ($CDCl_3$) (the asterisk indicates **5i**) δ=8.2, 9.4,* 32.6, 32.9,* 37.7, 48.8,* 75.4,* and 75.8. These assignments were supported for dibromo and dichloro analogs as follows: 1,2-dibromo-2-ethylbutane (**8i**), ^{13}C NMR ($CDCl_3$) δ=9.5, 33.8, 38.2, and 75.3; 1,2-dichloro-2-ethylbutane (**9i**), ^{13}C NMR ($CDCl_3$) δ=8.2, 31.8, 48.5, and 76.1.

A Mixture of 3-Bromo-2-chloro- and 2-Bromo-3-chloro-2-methylbutanes (4j and 5j) from 2-Methyl-2-butene (3j): Bp 80—81°C/70 mmHg; MS M$^+$ *m/z* (rel intensity) 184, 186, and 188 (100:134:35); ^{1}H NMR ($CDCl_3$) δ=1.67—1.98 (9H, m) and 4.13—4.46 (1H, m); ^{13}C NMR ($CDCl_3$) (the asterisk indicates **5j**) δ=21.9,* 22.1, 27.0, 27.9,* 32.5, 33.2,* 58.4, 66.1,* 67.9,* and 71.6. These assignments were supported for dibromo and dichloro analogs as follows: 2,3-dibromo-2-methylbutane (**8j**), ^{13}C NMR ($CDCl_3$) δ=23.5, 28.0, 34.9, 59.4, and 68.2; 2,3-dichloro-2-methylbutane (**9j**), ^{13}C NMR ($CDCl_3$) δ=20.6, 26.5, 31.1, 65.2, and 71.3.

A Mixture of (*RS,SR*)-2-Bromo-3-chloro- and 3-Bromo-2-chloro-3-methylpentanes (4k and 5k) from (*E*)-3-Methyl-2-pentene (3k): Bp 68—69°C/48 mmHg; MS M$^+$ *m/z* (rel intensity) 198, 200, and 202 (100:134:28); ^{1}H NMR ($CDCl_3$) δ=0.93—1.18 (3H, m), 1.63—2.03 (8H, m), and 4.31 (1H, q, J=6.7 Hz); ^{13}C NMR ($CDCl_3$) (the asterisk indicates **5k**) δ=8.6, 9.8,* 21.7, 21.8,* 24.6, 25.2,* 36.6, 36.9,* 55.6, 63.0,* 74.4,* and 76.1. These assignments were supported for dibromo and dichloro analogs as follows: (*RS,SR*)-2,3-dibromo-3-methylpentane (**8k**), ^{13}C NMR ($CDCl_3$) δ=9.8, 23.2, 25.9, 38.4, 56.2, and 74.9; (*RS,SR*)-2,3-dichloro-3-methylpentane (**9k**), ^{13}C NMR ($CDCl_3$) δ=8.4, 20.3, 23.8, 35.2, 62.5, and 75.8.

A Mixture of (*RS,RS*)-2-Bromo-3-chloro- and 3-Bromo-2-chloro-3-methylpentanes (4l and 5l) from (*Z*)-3-Methyl-2-pentene (3l): Bp 70—71°C/48 mmHg; MS M$^+$ *m/z* (rel intensity) 198, 200, and 202 (100:132:35); ^{1}H NMR ($CDCl_3$) δ=0.93—1.18 (3H, m), 1.61—2.20 (8H, m), and 4.08—4.52 (1H, m); ^{13}C NMR ($CDCl_3$) (the asterisk indicates **5l**) δ=8.8, 9.9,* 21.5,* 21.8, 27.8, 28.7*, 32.3, 32.7,* 58.8, 66.0,* 74.7,* and 76.1. These assignments were supported for dibromo and dichloro analogs as follows: (*RS,RS*)-2,3-dibromo-3-methylpentane (**8l**), ^{13}C NMR ($CDCl_3$) δ=10.0, 23.0, 30.3, 32.4, 59.8, and 75.0; (*RS,RS*)-2,3-dichloro-3-methylpentane (**9l**), ^{13}C NMR ($CDCl_3$) δ=8.7, 20.4, 26.7, 31.8, 65.2, and 76.0.

A Mixture of 1-Bromomethyl-1-chloro- and 1-Bromo-1-(chloromethyl)cyclopentanes (4m and 5m) from Methylenecyclopentane (3m): Bp 42—43°C/5 mmHg; MS M$^+$ *m/z* (rel intensity) 196, 198, and 200 (100:132:34); ^{1}H NMR ($CDCl_3$) (the asterisk indicates **5m**) δ=1.52—2.26 (8H, m), 3.80, and 4.01* (2H, 2s); ^{13}C NMR ($CDCl_3$) (the asterisk indicates **5m**) δ=23.8, 40.6, 41.2, 52.2,* 74.9,* and 79.2. These assignments were supported for dibromo and dichloro analogs as follows: 1-bromo-1-(bromomethyl)cyclopentane (**8m**), ^{13}C NMR ($CDCl_3$) δ=23.9, 41.3, 41.4, and 74.9; 1-chloro-1-(chloromethyl)cyclopentane (**9m**), ^{13}C NMR ($CDCl_3$) δ=23.6, 39.8, 51.9, and 79.0.

A Mixture of 1-Bromomethyl-1-chloro- and 1-Bromo-1-(chloromethyl)cyclohexane (4n and 5n) from Methylenecyclohexane (3n): Bp 41—42°C/2 mmHg; MS M$^+$ *m/z* (rel intensity) 210, 212, and 214 (100:130:35); ^{1}H NMR ($CDCl_3$) (the asterisk indicates **5n**) δ=1.40—2.00 (10H, m), 3.68, and 3.92* (2H, 2s); ^{13}C NMR ($CDCl_3$) (the asterisk indicates **5n**) δ=22.1, 22.8,* 24.9, 37.3, 44.3, 55.2,* 72.5,* and 72.7. These assignments were supported for dibromo and dichloro analogs as follows: 1-bromo-1-(bromomethyl)cyclohexane (**8n**), ^{13}C NMR ($CDCl_3$) δ=23.0, 24.8, 38.0, 44.7, and 72.3; 1-chloro-1-(chloromethyl)cyclohexane (**9n**), ^{13}C NMR ($CDCl_3$) δ=21.8, 24.9, 36.4, 54.6, and 73.2.

Reaction of Alkenes 3a—n with 2. To a solution of **3** (12 mmol) in CH_2Cl_2 (50 ml) was added 5.5 ml of BrCl solution in CCl_4 (1.8 mol dm^{-3}) at 0°C over 5 min with stirring. After the solvent was removed under reduced pressure, the residues were analyzed by GLC and ^{13}C NMR. The results are given in Table 2. In all cases, GLC analyses showed the presence of 11—16% of dichloro adduct **9** and 13—19% of dibromo adduct **8** as by-products.

The reaction of 3,3-dimethyl-1-butene (**3e**) with **2** gave a

mixture of 1-bromo-2-chloro- and 2-bromo-1-chloro-3,3-dimethylbutane (**4e** and **5e**). The product composition of **4e** and **5e** was determined by ^{13}C NMR analysis: ^{13}C NMR ($CDCl_3$) (the asterisk indicates **5e**) δ=26.8, 27.6,* 35.2, 36.3,* 37.0, 47.6,* 68.8,* and 74.6. These assignments were supported for the ^{13}C NMR data of dibromo and dichloro adducts **8e** and **9e** as described above.

The reaction of methylenecyclopentane (**3m**) with **2** gave a mixture of 2-bromo-1-chloro- and 1-bromo-2-chloro-1-methylcyclopentane (**4o** and **5o**, 54.5%), 1-bromomethyl-1-chlorocyclopentane (**4m**, 11.0%), dichloro and dibromo adducts (25.5%), and unidentified products (9.0%), as determined by GLC analysis. Although no isolation of **4o** and **5o** was carried out, the retention time of GLC agreed with that of the sample prepared by the reaction of 1-methylcyclopentene (**3o**) with **1** as follows: Bp 42—43°C/5 mmHg; MS M^+ *m/z* (rel intensity) 196, 198, and 200 (100:131:32); ^1H NMR ($CDCl_3$) (the asterisk indicates **5o**) δ=1.90, 1.96* (2s), 1.70—3.10 (m), and 4.44—4.62 (m); ^{13}C NMR ($CDCl_3$) (the asterisk indicates **5o**) δ=20.8, 21.0,* 28.5,* 28.6, 34.9,* 35.4, 39.3, 40.6,* 62.6, 70.9,* 75.1,* and 79.5. The ratio of **4o** and **5o** was shown to be 86:14 by ^{13}C NMR analysis. This product ratio is close to the product ratio (**4o**:**5o**=83:17) for the reaction of **3o** with **2** under the same reaction conditions.

^1H NMR analysis of the recovered alkenes from the reaction of **3m** (20 mmol) with **2** (10 mmol) gave 67% of 1-methylcyclopentene (**3o**) and 33% of methylenecyclopentane (**3m**) as based on the relative areas of the signals at δ=5.30 and 4.83 for the olefinic protons, respectively.

The reaction of methylenecyclohexane (**3n**) with **2** also gave a mixture of 2-bromo-1-chloro- and 1-bromo-2-chloro-1-methylcyclohexanes (**4p** and **5p**, 7.5%), **4n** and **5n** (55.2%), and dichloro and dibromo adducts (37.3%), as determined by GLC analysis. Although no isolation of **4p** and **5p** was carried out, the retention time agreed with that of the sample prepared by the reaction of 1-methylcyclohexene (**3p**) with **1** as follows: Bp 41—42°C/2 mmHg; MS M^+ *m/z* (rel intensity) 210, 212, and 214 (100:134:34); ^1H NMR ($CDCl_3$) (the asterisk indicates **5p**) δ=1.75, 1.91* (2s), 1.56—2.60 (m), and 4.35—4.70 (m).

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