  Bull. Chem. Soc. Jpn., 57, 2111—2115 (1984)

Bromochlorination of Alkenes with Dichlorobromate(1−) Ion. I

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(Received October 12, 1983)

In the reaction of styrene with chlorine, the added bromide ions were mostly incorporated into the adduct, giving a bromo chloro compound. Tetrabutylammonium dichlorobromate(1−) was found to be an efficient bromochlorinating agent. The reactions of 2-butenes and stilbenes were completely *anti* stereospecific.

The reactions of alkenes with *N*-chlorosuccinimide (NCS) in the presence of a bromide ion have been know to proceed by prior formation of bromine chloride (BrCl) and its addition to alkenes.[1] Bromine chloride (BrCl) may presumably be produced from the reaction of molecular chlorine and a bromide ion.[2] On the other hand, quaternary ammonium dichlorobromate(1−) (R_4NBrCl_2) was prepared by treatment of quaternary ammonium bromide with chlorine.[3,4] The structure of R_4NBrCl_2 have been confirmed by IR and other spectral evidence.[4] No chemical reaction with R_4NBrCl_2, however, has been tried although a dichlorobromate(1−) ion has been accepted as an intermediate of the bromochlorination of alkenes.[1,5]

The reaction of alkene with R_4NBrCl_2 may proceed *via* BrCl as a possible intermediate, on assuming the following equilibrium (Scheme 1):

$$R_4N^+Br^- + Cl_2 \rightleftarrows R_4N^+BrCl_2^- \rightleftarrows R_4N^+Cl^- + BrCl$$

Scheme 1.

We investigated the reactions of alkenes with chlorine in the presence of tetrabutylammonium bromide and found that this system would be a convenient new bromochlorinating agent. We describe here the details of the reaction products obtained from reaction with styrene, the synthetic utility for bromochlorination, and also the mechanistic aspects of this reaction.

Results and Discussion

A solution of an excess amount of styrene (**1a**) in chloroform was treated at 15 °C with a chloroform solution of chlorine containing various amounts of tetrabutylammonium bromide. The reaction mixture was directly subjected to GLC analysis. The reaction products were a mixture of 1-chloro-2-phenylethylene (**2**), 1,2-dichloro-1-phenylethane (**3**), 2-bromo-1-chloro-1-phenylethane (**4a**), and 1,2-dibromo-1-phenylethane (**5**) with recovery of **1a**.

$$\underset{\mathbf{1a}}{C_6H_5CH{=}CH_2} \xrightarrow{Cl_2/Br^-} C_6H_5CH{=}CHCl\ (\mathbf{2}) + C_6H_5CHClCH_2Cl\ (\mathbf{3}) + C_6H_5CHClCH_2Br\ (\mathbf{4a}) + C_6H_5CHBrCH_2Br\ (\mathbf{5})$$

Scheme 2.

As was expected, the formation of the bromo chloro compound (**4a**) was markedly dependent on the amount of a bromide ion added (Table 1). The amount of **4a** increased proportionally with the increase of bromide ions until the number of bromide ions reached that of chlorine. Further addition of bromide ions moderately decreased the amount of **4a** with the formation of the dibromoalkane (**5**). Consequently, it is apparent that almost all the added bromide ions were incorporated into the adduct up to the equimolar amounts of bromide ions to that of chlorine. It is important to note that the ratios of **2** to **3** were nearly constant regardless of the numbers of bromide ions, and pretty close to that of the addition product of chlorine in the absence of bromide ions (Entry 1, Table 1).[6] In addition, only the bromo chloro adduct (**4a**) was formed in a regiospecific manner without contamination with 1-bromo-2-chloro-1-phenylethane, regardless of the number of bromide ions. The structure of the adduct (**4a**) was identified by comparison of its ^{13}C- and ^1H-NMR spectra with those of an authentic sample prepared from 1,2-dibromo-1-phenylethane and $SnCl_4$.[7]

If the bromochloroalkane (**4a**) was formed by the initial attack of chlorine, giving dichloride (**3**), and

TABLE 1. THE PRODUCT DISTRIBUTION[a] IN THE REACTION OF STYRENE (**1a**) WITH CHLORINE IN THE PRESENCE OF A BROMIDE ION[b] IN CHLOROFORM (50 ml) AT 15 °C

Entry	Added salt	Mol. ratio	%Composition[c]			
	mmol	Br^-/Cl_2	**2**	**3**	**4a**	**5**
1	no		45.7	54.3		
2	0.55	0.17	35.2	49.3	15.5	
3	0.80	0.25	34.4	42.5	23.1	
4	1.28	0.40	23.5	36.0	40.5	
5	1.95	0.61	14.1	23.1	62.8	
6	2.88	0.90	2.50	5.20	92.3	
7	3.22	1.01			100	
8	4.73	1.48			83.7	16.3

a) Determined by GLC analysis. b) Tetrabutylammonium bromide. c) Percentages are normalized to 100%. Values are not corrected for TCD response factors.

followed by either subsequent attack of a bromide ion on **3** or a 2-chloro-1-phenylethyl cation[8] as an intermediate, the ratios of **2** to **3** would be dependent on the amount of ammonium bromide. The present observations are inconsistent with the above mechanism and strongly suggest that the formation of **4a** is through a quite different mechanism from that of the process giving **2** and **3**. The most plausible process giving **4a** would involve an electrophilic attack of BrCl or dichlorobromate(1−) ion ($BrCl_2^-$) instead of chlorine. In fact, the reaction of BrCl to the same alkene has been found to yield only **4a** in a regiospecific manner.[9]

On the other hand, it is well known that the addition of molecular BrCl to alkene gives bromochloroalkane together with considerable amounts of dibromo and dichloro adducts formed by the attacks of Br_2 and Cl_2, which are in equilibrium with BrCl.[9,10] No dibromo and dichloro adducts were found in the present reaction by using an equimolar mixture of chlorine and bromide ion (Entry 7, Table 1). The results suggest that this reaction involves a different attacking species, not molecular BrCl. A similar result was also observed for the reaction of 3-β-trifluoroacetoxy-5-cholestene with BrCl in the presence of tetraphenylarsonium chloride, which gave the bromo chloro adduct in good yields without the formation of the dibromo and dichloro adducts.[11] In addition, kinetic data for the addition reaction of bromine to alkenes in the presence of a chloride ion have suggested a dichlorobromate(1−) ion as the reacting species.[5] Thus, a dichlorobromate(1−) ion would be the reactant and bromine chloride would not be involved in the process giving **4a**. A dichlorobromate(1−) ion was also suggested to be involved in the bromochlorination of cyclohexene with NCS and a bromide ion.[1]

As mentioned above, an equimolar mixture of chlorine and bromide ions would be a very effective and convenient bromochlorinating agent. Furthermore, several quaternary ammonium dichlorobromates(1−) were found to be easily isolable. The bromochlorinations of alkenes were also tried with the isolated salts. The reaction of styrene (**1a**) with tetrabutylammonium dichlorobromate(1−) (**6**) in chloroform completed within a few minutes at 0 °C, giving **4a** in nearly quantitative yield. Tetramethylammonium and phenyltrimethylammonium dichlorobromates(1−) (**7** and **8**) were also useful for the bromochlorination of alkenes, regardless of their lower solubilities. The reaction of **1a** with **6** was examined in several different solvents with a wide variety of polarities. Reactions in dioxane, carbon tetrachloride, ethyl acetate, dichloromethane, 1,2-dichloroethane, and acetic anhydride gave **4a** in similar yields. Thus, the usual aprotic solvents can be employed as the reaction medium. On the other hand, the reaction of **1a** in acetic acid gave **4a** (65%) and 1-acetoxy-2-bromo-1-phenylethane (**9**, 35%). In methanol, the major product was 2-bromo-1-methoxy-1-phenylethane (**10**, 80%). These results have also been found in the reaction of 1-hexene with BrCl in methanol.[12]

In order to obtain some information on the mechanistic aspects, the reactions of **6** with a variety of alkenes were examined. The results are given in Table 2. In analogy with the reaction of **1a**, reactions with methyl *trans*-cinnamate (**1b**) and vinyl acetate (**1c**) gave the corresponding regiospecific products. Addition to such alkenes as propene (**1d**) and 3-chloropropene (**1e**) gave both Markownikoff and *anti*-Markownikoff adducts. The reason for the formation of *anti*-Markownikoff adducts is uncertain; however, it may be attributed to the combined effects of polar and steric effects. Similar orientation have also been found in the reactions of these alkenes with other bromochlorinating agents.[13,14]

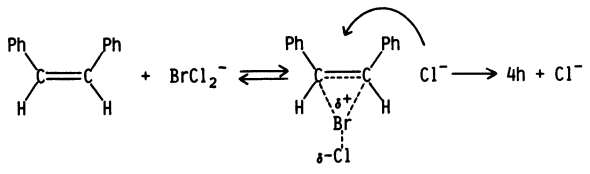
The additions to *cis*- and *trans*-2-butenes (**1f** and **1f'**), cyclohexene (**1g**), and methyl *trans*-cinnamate (**1b**) with **6** gave completely *anti* stereospecific products. Similarly, *anti* stereospecific products, *threo*- and *erythro*-1-bromo-2-chloro-1,2-diphenylethanes (**4h** and **4h'**) were obtained from *cis*- and *trans*-stilbenes (**1h** and **1h'**), respectively. The solvent effect on *anti*

Table 2. Bromochlorination of alkenes with **6** in $CHCl_3$[a]

Alkenes	Temp /°C	Products	Yield/%[b]
1a	0	$C_6H_5CHClCH_2Br$ (**4a**)	85(97)
1a	15	**4a**	84(98)[c]
1a	15	**4a**	86(95)[d]
1b	70	$C_6H_5CHClCHBrCOOMe$ (**4b**)	85[e]
1c	−5	$CH_2BrCHClOCOCH_3$ (**4c**)	82
1d	0	$CH_2BrCHClCH_3$ (**4d**)	85[f]
		$CH_2ClCHBrCH_3$ (**4d'**)	
1e	50	$CH_2BrCHClCH_2Cl$ (**4e**)	82[g]
		$CH_2ClCHBrCH_2Cl$ (**4e'**)	
1f	−10	$CH_3CHBrCHClCH_3$ (**4f**)	84[h]
1f'	−10	$CH_3CHBrCHClCH_3$ (**4f'**)	85[e]
1g	0	$C_6H_{10}BrCl$ (**4g**)	85[i]
1h	20	$C_6H_5CHBrCHClC_6H_5$ (**4h**)	95[h]
1h'	20	$C_6H_5CHBrCHClC_6H_5$ (**4h'**)	97[e]
1i	70	EtOOCCHBrCHClCOOEt (**4i'**)	66[e]
1i'	70	EtOOCCHBrCHClCOOEt (**4i'**)	71[e]

a) Reactions were carried out with 30 mmol of **6**, 30 mmol of alkene, and 100 ml of $CHCl_3$. b) Isolated yield. Figures in parentheses represent product yields determined by ^1H NMR before isolation using ethylbenzene as the internal standard. c) **7** as bromochlorinating agent. d) **8** as bromochlorinating agent. e) *erythro*. f) **4d**:**4d'**=56:44. g) **4e**:**4e'**=31:69. h) *threo*. i) *trans*.

stereospecific addition was examined. The reactions of **1h** in dichloromethane, 1,2-dichloroethane, acetic anhydride, and nitromethane gave *threo* isomer (**4h**) free from *erythro* isomer (**4h'**). In contrast, it has previously been reported that the addition of molecular BrCl to **1h'** in chloroform is *anti* stereospecific, while that of **1h** gives considerable amounts of **4h'**.[9] Furthermore, the stereochemistry of bromine addition to **1h** has been known to be dependent on the solvents.[15] Thus, the mode of the reaction is very different in the additions to **1h** with **6** and with BrCl (and Br_2). Therefore, the present results cannot be explained on the basis of any accepted mechanism for the additions of bromine and bromine chloride.[15,16] The completely *anti* stereospecific addition with **6** can be explained by assuming an $AdEC_2$-type mechanism involving a rate- and product-determining attack of a chloride ion to a three-center bound π complex-type intermediate (**11**)[17], as shown in Scheme 3. A similar mechanism has been suggested for the additions of Br_3^- and Br_2Cl^- to alkenes and dienes.[16,18]



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Scheme 3.

The product obtained from diethyl maleate (**1i**) and fumarate (**1i'**) was the same compound, diethyl *erythro*-2-bromo-3-chlorosuccinate (**4i'**). The reactions with these electron-deficient alkenes proceeded only on heating and the maleate (**1i**) was found to isomerize to the fumarate (**1i'**) under the reaction conditions. On the other hand, fumaric and maleic acids have been known to react with BrCl, yielding *erythro*- and *threo*-2-bromo-3-chlorosuccinic acids, respectively.[19] The difference would be additional evidence to support the conclusion that the reactant in the reaction of **6** is not BrCl but $BrCl_2^-$.

When compared with other bromochlorinating agents, the merits of ammonium dichlorobromate(1−) become evident. Although the formation of bromochloroalkanes by the use of a mixture of Br_2 and Cl_2 has been well known,[9] the yields appeared to be lower due to contaminations of dichloro and dibromoalkanes. Certain olefinic substances with BrCl prepared *in situ* from *N*-bromoacetamide and hydrogen chloride also give undesired by-products,[7] as was the case for a mixture of NCS and a bromide ion.[1] Although pyridine-BrCl complex[16,20] and a mixture of Br_2 and $SbCl_5$ (or $SbCl_3$)[13] were reported to be effective bromochlorinating agents, the products were usually complex. Tetraalkylammonium dichlorobromate(1−) can be handled easily and can be used as a very convenient bromochlorinating agent. Simple purification of the product provides pure bromochloroalkane in nearly quantitative yield.

Experimental

All the melting points and boiling points are uncorrected. NMR spectra were recorded on a JEOL JNM FX-60Q and a JEOL C-60HL spectrometer, using TMS as an internal standard. Mass spectra were recorded on a JMS-D-300 Mass spectrometer. The GLC analyses were performed on a Yanako GCG-550T with a Silicon DC 550 (25%)-Celite 545 (2 m) column (A) or Yanako G-180 Gas Chromatograph with a High vacuum silicon grease (25%)-Celite 545 (2 m) column (B). All the organic starting materials, including the solvents, were distilled or recrystallized before use. Chlorine was passed through water and sulfuric acid. Tetrabutylammonium dichlorobromate(1−) (**6**), tetramethylammonium dichlorobromate(1−) (**7**), and phenyltrimethylammonium dichlorobromate(1−) (**8**) were prepared by the literature procedure.[3]

The Reaction of Styrene (1a) with Chlorine in the Presence of Tetrabutylammonium Bromide. Experiments were carried out by adding 20 ml of chlorine solution in chloroform (0.16 mol dm^{-3}) in the presence of various amounts of tetrabutylammonium bromide (0.55—4.73 mmol) to 6.4 mmol of **1a** (in 30 ml of the same solvent) at 15 °C with stirring for 10 min. After the reaction completed, the mixture was washed with aq Na_2CO_3 and water, and dried over $MgSO_4$. The solvent was removed by evaporation. The relative amounts of products were determined by the peak areas of GLC on the column (A) at 100 °C with hydrogen as a carrier gas (50 ml/min). Retention times (in minutes) were: **1a**, 1; **2**, 3.2; **3**, 7.8; **4a**, 12.8; **5**, 14. The results are given in Table 1.

The Reaction of Styrene (1a) with 6. General Procedure: To a solution of **1a** (3.12 g, 30 mmol) in chloroform (100 ml), was added **6** (11.8 g, 30 mmol) at 0 °C over 20 min with stirring. The mixture was stirred for an additional 10—20 min, then washed with five 100-ml portions of water to remove the ammonium salt, dried over Na_2SO_4, and the solvent was evaporated. Distillation afforded 5.6 g (85%) of pure **4a**: bp 80—81 °C/1 mmHg (1 mmHg≈133.322 Pa) (lit,[7] 106—107 °C/6 mmHg); ^1H NMR ($CDCl_3$) δ=3.82, 3.83 (2H, 2d, J=8.3 and 6.6 Hz, CH_2Br), 5.03 (1H, q, J=8.3 and 6.6 Hz, CHCl), 7.36 (5H, s, C_6H_5); ^{13}C NMR ($CDCl_3$) δ=35.9, 61.3, 127.2, 128.6, 129.0, 138.3; MS M^+ at m/z=218, 220, 222 (100:129:34); Found: m/z 217.9494. Calcd for C_8H_8BrCl: M, 217.9499. Yields in other aprotic solvents were: in dioxane, 78%; CCl_4, 80%; $CH_3COOC_2H_5$, 79%; CH_2Cl_2, 85%; CH_2ClCH_2Cl, 83%; $(CH_3CO)_2O$, 80%.

In Acetic Acid as the Solvent. To a solution of **1a** (1.04 g, 10 mmol) in acetic acid (30 ml) was added **6** (3.93 g, 10 mmol) at 20 °C over 5 min with stirring. The product was isolated by pouring the reaction mixture into cold saturated aq NaCl, followed by extraction with ether (200 ml) and washing with aq $NaHCO_3$ and water. The ethereal extract was dried over $MgSO_4$ and concentrated. The residue (2.00 g) was analyzed by GLC and ^1H-NMR. The composition analyzed by GLC was: **4a**, 65.4 and 1-acetoxy-2-bromo-1-phenylethane (**9**), 34.6%. ^1H-NMR shows 67:33 mixture of **4a** and **9**, respectively (by integration of methine protons). The ^1H-NMR spectrum of **9** corresponds well with that reported in the literature.[21]

In Methanol as the Solvent. To a solution of **1a** (1.04 g, 10 mmol) in methanol (30 ml) was added **6** (3.93 g, 10 mmol) at 0 °C over 5 min with stirring. The solvent was removed by evaporation, and ether (150 ml) was added to the residue. The ether solution was washed with aq $NaHCO_3$ and water. The ethereal extract was dried over $MgSO_4$ and concentrated. ^1H-NMR spectrum of the residue shows a 80:20 mixture of 2-bromo-1-methoxy-1-phenylethane (**10**) and **4a**, respectively (by integration of methine protons). Column chromatography of the residual oil (1.85 g) on silica gel with hexane as the eluent gave 1.10 g of pure **10** and 0.2 g of **4a**. The data for **10** are as follows: bp 65—66 °C/2 mmHg (lit,[22] 57 °C/0.40 mmHg); ^1H NMR ($CDCl_3$) δ=3.32 (3H, s, CH_3), 3.49,

3.50 (2H, 2d, J=5.7 and 7.0 Hz, CH_2Br), 4.37 (1H, approx. triplet, CH), 7.35 (5H, s, C_6H_5); ^{13}C NMR ($CDCl_3$) δ=36.2, 57.2, 83.4, 126.7, 128.4, 128.6, 139.0; MS M^+ at m/z=214, 216 (100:96); Found: m/z 213. 9981. Calcd for $C_9H_{11}BrO$: M, 213.9994.

Syntheses of Bromochloroalkanes by ***6*** *in Chloroform.* The procedure was the same as that described for that of **1a**, except for the reaction temperature and period. The results are given in Table 2.

Methyl erythro-*2-bromo-3-chloro-3-phenylpropanate (**4b**).* Mp 118—120 °C (from pentane). ^1H NMR ($CDCl_3$) δ=3.89 (3H, s, CH_3), 4.62 (1H, d, J=11.3 Hz, CHBr), 5.27 (1H, d, J=11.3 Hz, CHCl), 7.39 (5H, s, C_6H_5). Found: C, 43.51; H, 3.37%. Calcd for $C_{10}H_{10}BrClO_2$: C, 43.27; H, 3.63%.

*1-Acetoxy-2-bromo-1-chloroethane (**4c**).* Bp 80—81 °C/25 mmHg (lit,[13] 64—65 °C/10 mmHg). ^1H NMR ($CDCl_3$) δ=2.17 (3H, s, CH_3), 3.70 (2H, d, J=6.0 Hz, CH_2Br), 6.53 (1H, t, J=6.0 Hz, CHCl). ^{13}C NMR ($CDCl_3$) δ=20.6, 32.7, 80.0, 168.0.

*1-Bromo-2-chloropropane (**4d**) and 2-Bromo-1-chloropropane (**4d'**).* Gaseous propene (**1d**) from a cylinder was passed through the chloroform solution of **6** at 0 °C until the yellow color disappeared. After the usual work-up procedure, mixed bromochloroalkanes (**4d** and **4d'**) were obtained: bp 53—55 °C/70 mmHg. ^1H-NMR shows a 56:44 mixture of **4d** and **4d'**, respectively. ^1H NMR ($CDCl_3$) (an asterisk indicates **4d**) δ=1.65* (d, J=6.35 Hz, CH_3), 1.79 (d, J=6.34 Hz, CH_3), 3.3—4.4 (m). ^{13}C NMR ($CDCl_3$) (an asterisk indicates **4d**) δ=23.2, 37.5*, 46.3, 49.6, 55.4*. Although attempts to separate two regioisomers were unsuccessful, these assignments were supported for dibromo and dichloro analogs.[23]

*1-Bromo-2,3-dichloropropane (**4e**) and 2-Bromo-1,3-dichloropropane (**4e'**).* A mixture of two isomeric bromodichloropropanes (**4e** and **4e'**) was obtained from 3-chloropropene (**1e**): bp 60—62 °C/22 mmHg. ^{13}C NMR shows a 31:69 mixture of **4e** and **4e'**, respectively. The ratio was obtained by comparison of the spectra of each pure sample as follows: **4e**, ^{13}C NMR ($CDCl_3$) δ=33.1, 46.0, 57.9; **4e'**, ^{13}C NMR ($CDCl_3$) δ=45.2, 49.1.

threo-*2-Bromo-3-chlorobutane (**4f**).* Bp 45—48 °C/30 mmHg (lit,[24] 50—52 °C/30 mmHg). ^1H NMR ($CDCl_3$) δ=1.60 (3H, d, J=6.6 Hz, CH_3), 1.74 (3H, d, J=6.6 Hz, CH_3), 4.0—4.8 (2H, m, CHCl and CHBr). ^{13}C NMR ($CDCl_3$) δ=20.3, 20.4, 52.5, 60.5. MS M^+ at m/z=170, 172, 174 (100:129:31). Found: m/z 169.9490. Calcd for C_4H_8BrCl: M, 169.9498.

erythro-*2-Bromo-3-chlorobutane (**4f'**).* Bp 51—52 °C/50 mmHg (lit,[24] 50—52 °C/51 mmHg). ^1H NMR ($CDCl_3$) δ=1.65 (3H, d, J=6.3 Hz, CH_3), 1.80 (3H, d, J=6.5 Hz, CH_3), 4.0—4.3 (2H, m, CHBr and CHCl). ^{13}C NMR ($CDCl_3$) δ=23.5, 53.8, 61.8. MS M^+ at m/z=170, 172, 174 (100:131:33). Found: m/z 169.9495. Calcd for C_4H_8BrCl: M, 169.9498.

trans-*1-Bromo-2-chlorocyclohexane (**4g**).* Bp 91—92 °C/18 mmHg (lit,[13] 90—95 °/17 mmHg). ^{13}C NMR ($CDCl_3$) δ=22.5, 23.3, 32.8, 33.3, 55.5, 62.9. MS M^+ at m/z=196, 198, 200 (100:129:32). Found: m/z 195.9640. Calcd for $C_6H_{10}BrCl$: M, 195.9655. The ^1H-NMR spectrum corresponds well with that reported in the literature.[25]

threo-*1-Bromo-2-chloro-1,2-diphenylethane (**4h**).* Mp 102.5—103 °C (from 95% ethanol) (lit,[9] 99—100 °C). ^1H NMR ($CDCl_3$) δ=5.34 (2H, s, CHBr and CHCl), 7.18 (10H, s, $2C_6H_5$). MS M^+ at m/z=294, 296, 298 (100:127:32). Found: m/z 293.9819. Calcd for $C_{14}H_{12}BrCl$: M, 293.9811.

erythro-*1-Bromo-2-chloro-1,2-diphenylethane (**4h'**).* Mp 218—221 °C (from ligroine) (lit,[9] 220—221 °C). ^1H NMR ($CDCl_3$) δ=5.32 (2H, s, CHBr and CHCl), 7.42 (10H, m, $2C_6H_5$). MS M^+ at m/z=294, 296, 298 (100:132:34). Found: m/z 293.9809. Calcd for $C_{14}H_{12}BrCl$: M, 293.9811.

*The Reactions of Diethyl Fumarate (**1i'**) and Maleate (**1i**) with **6**.* The mixture of **6** (11.8 g, 30 mmol) and **1i'** (5.16 g, 30 mmol) in 100 ml of $CHCl_3$ was stirred at refluxing temperature for 50 h. The reaction mixture was washed with aq Na_2SO_3 and water. After the usual work-up procedure, the solid residue was recrystallized from ligroine to give 6.15 g (71%) of diethyl *erythro*-2-bromo-3-chlorosuccinate (**4i'**, mp 56—57 °C). The structure was confirmed by comparison of the ^1H-NMR spectra with that reported in the literature.[13]

In a similar way, analysis of the residue from the reaction of **1i** with **6** by ^1H-NMR revealed a mixture of **4i'** and unreacted alkenes. The solid residue was recrystallized from ligroine to give 5.7 g (66%) of product (mp 56—57 °C) (not depressed on admixture with the product obtained from **1i'**). ^1H-NMR analysis of the recovered alkene indicated 77% of **1i'** and 23% of **1i** on the basis of relative areas of the signals at δ=6.84 and 6.25 for olefinic protons, respectively.

Reaction of cis-*Stilbene (**1h**) with **6** in Various Solvents.* The reactions were carried out by the addition of 2 mmol of **6** to 2 mmol of **1h** in 50 ml of the solvents at 20 °C with stirring. After the yellow color disappeared, the reaction mixture was washed with water and dried over Na_2SO_4. The product of the reaction in acetic anhydride was isolated by extraction with ether. After the solvent was removed under reduced pressure, the residue was analyzed by GLC and ^1H-NMR. Reactions in $CHCl_3$, CH_2Cl_2, CH_2ClCH_2Cl, $(CH_3CO)_2O$, and CH_3NO_2 gave *threo* isomer (**4h**) free from *erythro* isomer (**4h'**). Yields in the solvents were: in $CHCl_3$, 95%; CH_2Cl_2, 98%; CH_2ClCH_2Cl, 96%; $(CH_3CO)_2O$, 95%; CH_3NO_2, 95%. The GLC analysis was performed on the column (B) at 150 °C with helium as a carrier gas (50 ml/min).

The authors wish to thank Dr. Seizi Kozuka of Osaka City University for helpful discussions.

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