The Chlorobromination of Olefins with Antimony (III and V) Chlorides

Sakae Uemura,* Akira Onoe, and Masaya Okano
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611

(Received June 5, 1973)

By the reaction of olefins with equimolar mixtures of $SbCl_5$ and Br_2 or LiBr, and of $SbCl_3$ and Br_2, in carbon tetrachloride, various bromochloroalkanes were obtained in good yields. The mixtures of certain metal chlorides of the Lewis acid type (*e.g.*, $FeCl_3$, $SnCl_4$, and $TiCl_4$) and Br_2 could also be used as chlorobrominating agents, but these mixtures were found to be inferior to the $SbCl_5$–Br_2 mixture in product selectivities.

The *in situ* formation of ICl and its addition to olefins, by the use of mixtures consisting of certain metal chlorides (*e.g.*, AgCl, $HgCl_2$, CuCl, *etc.*) and I_2

$$MCl_n + I_2 \longrightarrow MCl_{n-1}I + ICl \quad (1)$$

[Eq. (1)], have been known for a long time.[1] Baird *et al.* have recently found a more efficient system containing $CuCl_2$, in which the oxidation of the iodide anion with the copper(II) salt is involved and a com-

$$2CuCl_2 + I_2 \longrightarrow 2CuCl + 2ICl \quad (2)$$

plete utilization of I_2 is achieved [Eq. (2)].[2)] A similar chlorobromination using the $CuCl_2$–Br_2 mixture, however, appears to be less satisfactory in yield and product selectivity.[2b)] Though a mixture of bromine and chlorine has also been used as a source of BrCl, the reported yields of bromochloroalkanes are not very high.[3)] During the studies of halogenation reactions with $SbCl_5$, we have found convenient new chlorobrominating agents consisting of $SbCl_5$ or $SbCl_3$ and Br_2. When various olefins were treated with these equimolar mixtures in carbon tetrachloride, bromochloroalkanes were obtained in good yields, just as when the mixture of *N*-bromoacetamide and hydrogen chloride was used.[4)] This paper will describe some results of mixed halogenations with these metal chloride–halogen mixtures.

Results and Discussion

The reaction of cyclohexene with an equimolar mixture of $SbCl_5$ and Br_2 in carbon tetrachloride was completed at room temperature within a few minutes. Some other metal chlorides which were soluble in carbon tetrachloride were also examined as chloride components under somewhat different reaction conditions. In these reactions, *trans*-1-bromo-2-chlorocyclohexane was generally obtained in good yields, together with smaller amounts of *trans*-1,2-dibromocyclohexane. All the results are given in Table 1a. As can be seen from the table, the $SbCl_5$–Br_2 mixture in carbon tetrachloride was found to be superior to the other ones in yield and in product selectivity. Dichloroethane could be used as an effective solvent, but the use of carbon disulfide resulted in less satisfactory results (compare Runs 1—3 in Table 1a).

When $SbCl_5$ was used as a chloride component, nearly two moles of the bromochloride were formed from one mole of Br_2; hence, the stoichiometry of the reaction is given by Eq. (3).

$$2C_6H_{10} + SbCl_5 + Br_2 \longrightarrow 2C_6H_{10}BrCl + SbCl_3 \quad (3)$$

Here, the generation of two moles of BrCl can be rationalized by assuming the following successive reactions [Eqs. (4) and (5)].

$$SbCl_5 + Br_2 \rightleftharpoons BrCl + SbCl_4Br \quad (4)$$

$$SbCl_4Br \rightleftharpoons BrCl + SbCl_3 \quad (5)$$

Since the BrCl formation of the former type is similarly observed for certain metal chlorides (see below), the presumed participation of Eq. (4) may not be unreasonable. The latter reductive dissociation may be anticipated from the favorable reduction potential of Sb(V)[5)] and facilitated by the presence of the more electropositive bromine atom in the ligands,[6)] but the reverse reaction does not seem to be easy. Thus, the overall reaction [(4)+(5)] would be highly in favor of the BrCl formation. In connection with this a similar observation has been reported in the literature[7)] that $SbCl_5$ reacted with I_2 to afford ICl and $SbCl_3$ and that no isolation of $SbCl_4I$ was achieved. Another possibility, that of BrCl formation from Br_2 and Cl_2 (liberated from $SbCl_5$), can be excluded, because Cl_2 generation has not been observed in the chlorination of olefins with $SbCl_5$ under similar reaction conditions.[8)]

Though the *in situ* formation of BrCl in this reaction is highly probable, as has been described above, its attacking form is not decisive. The following observation, however, appears to suggest that the attacking entity is the BrCl molecule itself (probably somewhat activated by $SbCl_5$ or $SbCl_3$). In the competitive bromination of benzene and toluene with the $SbCl_5$–Br_2 mixture under the same conditions (in CCl_4 at 25 °C), a considerably high selectivity (k_T/k_B value) was observed;[9)] this selectivity was slightly less than that for the attack of the Br_2 molecule itself.

On the other hand, when other metal chlorides of the Lewis acid type, such as $FeCl_3$, $SnCl_4$, and $TiCl_4$, were used as chloride components, nearly one (but not more than one) mole of the mixtures of the bromochloride and dibromide, with the amount of the former being dominant, were obtained from one mole of Br_2 (Runs 4—6 in Table 1a). Further, in the halogenation with the $FeCl_3$–Br_2 mixture, it was confirmed that the reaction was accompanied by almost no reduction of the Fe(III) cation (<10% by iodometry). The oxidations of Br^- with the above metal chlorides (except for $SbCl_5$) were also not observed appreciably (see below). These results seem natural because of the very low reduction potentials of the metal cations. The *in situ* BrCl formation was similarly observed even in the case

Table 1. Chlorobromination and chloroiodination of cyclohexene in carbon tetrachloride
cyclohexene (100 mmol)

Run	Metal chloride mmol	Halogen donor mmol	Solvent ml	Temp. °C	Time min	Products[a)] Chlorohalide mmol (yield[b)] %; selectivity %)	Products[a)] Other halide mmol
	(a) Chlorobromination						
1	$SbCl_5$ 25	Br_2 25	100	30	5	47.9 (96; 98)	diBr 0.4; diCl 0.6
2	$SbCl_5$ 25	Br_2 25	100[c)]	30	5	46.5 (93; 97)	diBr 0.9; diCl 0.5
3	$SbCl_5$ 25	Br_2 25	100[d)]	30	5	42.9 (86; 89)	diBr 5.3; diCl 0.1
4	$FeCl_3$ 50	Br_2 25	150	76	10	17.6 (70; 72)	diBr 7.0
5	$SnCl_4$ 50	Br_2 25	100	25	5	21.6 (86; 87)	diBr 3.2
6	$TiCl_4$ 50	Br_2 25	100	5	10	18.8 (75; 75)	diBr 6.2
7	$SbCl_3$ 50	Br_2 25	100	76	10	20.0 (80; 82)	diBr 4.4
8	$SbCl_3$ 52	Br_2 50	100	76	10	31.7 (63; 71)	diBr 13.0
9	$SbCl_5$ 25	LiBr 12.5	150	76	5	6.1 (49; 32)	diCl 12.9
10	$SbCl_5$ 25	LiBr 25	150	76	5	20.3 (81; 95)	diCl 1.2
11	$SbCl_5$ 25	LiBr 37.5	150	76	5	14.1 (56; 94)	diBr 1.0
12	$FeCl_3$ 50	LiBr 50	150	76	60	1.2 (2)	—
	(b) Chloroiodination						
	$SbCl_5$ 25	I_2 25	200	76	10	47.0 (94)[e)]	
	$SnCl_4$ 25	I_2 25	100	76	10	23.7 (95)[e)]	
	$SbCl_3$ 50	I_2 50	300	76	180	36.8 (74)[e)]	
	$SbCl_5$ 25	LiI 27	100	76	10	23.4 (94)[e)]	

a) Yields were determined by glc.
b) Based on Eq. 3 for $SbCl_5$–Br_2 couple, Eq. 7 for MCl–Br_2 couple, and Eq. 9 for $SbCl_5$–LiBr couple, respectively.
c) Solvent, dichloroethane.
d) Solvent, carbon disulfide.
e) Isolated yield.

of a low-valence compound, $SbCl_3$ (see Runs 7 and 8). Thus, it seems very likely that BrCl is formed by the

$$MCl_n + Br_2 \rightleftharpoons BrCl + MCl_{n-1}Br \qquad (6)$$

halogen exchange reaction [Eq. (6)], though no direct evidence for the formation of the mixed metal halide is available at present. Since it is known that all these metal chlorides have a considerable affinity for Cl^-,[10)] this transformation may proceed *via* an ionic adduct intermediate, *e.g.*, $Br^+[FeCl_3Br]^-$. The stoichiometry of the halogenation using the mixtures of these metal chlorides and Br_2 may be expressed by Eq. (7).

$$C_6H_{10} + MCl_n + Br_2 \longrightarrow C_6H_{10}BrCl + MCl_{n-1}Br \qquad (7)$$

The formation of the by-product, *trans*-1,2-dibromocyclohexane, can be explained in terms of the attack of Br_2, which is equilibrated [*cf.* Eq. (6)].

Furthermore, when various metal chlorides were mixed with LiBr in carbon tetrachloride and the mixtures (slightly heterogeneous, probably because of the lower solubility of the LiCl formed) were treated with cyclohexene, no significant red-coloration (due to the generation of BrCl) and no, or only a slight, formation of 1-bromo-2-chlorocyclohexane was observed, except only for the case of $SbCl_5$ (see Runs 9—12 in Table 1a). In the $SbCl_5$–LiBr system, the use of an equimolar mixture of both salts was required for the chlorobromination. Perhaps the BrCl[11)] may arise from the mixed pentahalide formed by means of Eq. (8) and

$$SbCl_5 + LiBr \rightleftharpoons Li^+[SbCl_5Br^-] \rightleftharpoons LiCl + SbCl_4Br \qquad (8)$$

$$SbCl_4Br \rightleftharpoons BrCl + SbCl_3 \qquad (5)$$

$$C_6H_{10} + SbCl_5 + LiBr \longrightarrow C_6H_{10}BrCl + SbCl_3 + LiCl \qquad (9)$$

the stoichiometry of the reaction may be represented by Eq. (9). Excess $SbCl_5$ caused a considerable formation of *cis*- and *trans*-1,2-dichlorocyclohexanes as by-products,[8)] and excess LiBr resulted in contamination with the dibromide [see Eq. (10)]. In addition, the use of KBr instead of LiBr was not successful because of its lower solubility in the solvent.

$$BrCl + LiBr \rightleftharpoons Br_2 + LiCl \qquad (10)$$

The method using $SbCl_5$ or $SbCl_3$ as a chloride source was found to be applicable to the chloroiodination of olefins. The data for cyclohexene are given in Table 1b. Though somewhat severe reaction conditions were required as compared to those in the chlorobromination, the yield was satisfactory. Both our results and Baird's data show that, in the chlorobromination, some competitive bromination always occurred, the quantity depending on the combination of metal chlorides and bromine, whereas in the chloroiodination no competitive iodination was observed. Such trends may be reasonably explained by differences in the reactivities between halogens and interhalogens (reported relative rates for the addition to olefins in acetic acid:[12)] BrCl: Br_2=400: 1, ICl: I_2=10^5: 1). The use of $SnCl_4$ instead of $SbCl_5$ or $SbCl_3$ was also successful, but the system containing $FeCl_3$ was ineffective.

The chlorobromination of various olefins other than

TABLE 2. CHLOROBROMINATION OF VARIOUS OLEFINS IN CARBON TETRACHLORIDE
olefin (50—100 mmol); halogenating agent A, $SbCl_5$ (25 mmol)+Br_2(25 mmol), B, $SbCl_3$ (50—100 mmol)+Br_2(50 mmol); solvent (100—200 ml)

Olefin	Halogenating agent	Temp. °C	Time min	Product (yield %)[a]	
$C_6H_{13}CH{=}CH_2$	B	76	10	$C_6H_{13}CHClCH_2Br$(I) $C_6H_{13}CHBrCH_2Cl$(II)	(73)[b,c]
$C_6H_5CH{=}CH_2$	B	0	10	$C_6H_5CHClCH_2Br$	(87)
trans-$C_6H_5CH{=}CHC_6H_5$	A	45	10	$C_6H_5CHClCHBrC_6H_5$	(74)[d]
$CH_2{=}CHOAc$	A	5	10	$CH_2BrCHCl(OAc)$	(79)
trans-$C_6H_5CH{=}CHCOOEt$	A	76	10	$C_6H_5CHClCHBrCOOEt$	(73)[d]
$CH_2{=}CHCH_2Cl$	B	76	10	$CH_2ClCHBrCH_2Cl$(I) $CH_2BrCHClCH_2Cl$(II)	(71)[e]
$CH_2{=}CHCH_2Br$	B	76	10	$CH_2ClCHBrCH_2Br$(I) $CH_2BrCHClCH_2Br$(II)	(83)[e]
cis-$CHCl{=}CHCl$	A	76	60	$CHClBrCHCl_2$	(77)
trans-$CHCl{=}CHCl$	A	76	60	$CHClBrCHCl_2$	(75)
cis-$EtOOCCH{=}CHCOOEt$	A	76	60	$EtOOCCHBrCHClCOOEt$	(52)[f]
trans-$EtOOCCH{=}CHCOOEt$	A	76	60	$EtOOCCHBrCHClCOOEt$	(66)[d]

a) Isolated yield.
b) I: II=7: 3 (glc, Gorey column (BDS, 90 m)).
c) By-product, dibromide (20%).
d) *erythro.*
e) I: II=*ca.* 7: 3 (IR).
f) *threo.*

cyclohexene was easily achieved by the use of mixtures of $SbCl_5$ or $SbCl_3$ and Br_2. Unsymmetrical olefins, such as 1-octene and allyl chloride or bromide, yielded mixtures of the Markownikov and *anti*-Markownikov adducts. 1-Octene afforded the former adduct predominantly, while the reverse was found for allyl halides. Such an abnormal orientation has also been found in the reaction of allyl halides with HOCl; it can be explained by neighbouring group participation.[13] Styrene, vinyl acetate, and ethyl cinnamate gave only products in accordance with Markownikov's rule, as anticipated on the basis of electronic and steric effects. For certain olefins, the $SbCl_3$–Br_2 mixture would be useful—*e.g.*, the use of $SbCl_5$ resulted in a decrease in the product selectivity in the reaction with 1-octene and a considerable formation of a tarry product in the reaction with styrene.

Experimental

Materials. All the organic starting materials, including the solvents, were distilled before use. Commercial metal halides, Br_2, and I_2 (best grade) were used without further purification.

Reaction of Cyclohexene with Metal Chlorides and Bromine Donors. To a nearly homogeneous solution of a metal chloride (25 or 50 mmol) and Br_2 or LiBr (25 or 50 mmol) in CCl_4 (100 or 150 ml), cyclohexene (100 mmol) was gradually added at the prescribed temperature. After stirring was continued for a definite period, the reaction mixture was treated with water, and the inorganic precipitate thus formed was removed by filtration. The CCl_4 layer was separated from the aqueous one, and the solvent was evaporated. A liquid fraction boiling at 91—95 °C/17 mmHg was collected; it consisted of *trans*-1-bromo-2-chlorocyclohexane and *trans*-1,2-dibromocyclohexane, and occasionally also *cis*- and *trans*-1,2-dichlorocyclohexanes. The structural confirmation of these products was made by a comparison of the NMR spectra with those reported in the literature.[14] The composition of the above fraction was determined by means of the glc analysis [apparatus, Shimadzu 5APTF; columns, PEG 6000 (25%)-Chromosorb W(3m), Silicon D.C. 550 (25%)-Shimalite (3m), and Apiezon L(30%)-Celite (1m); carrier gas, N_2].

Syntheses of Bromochloroalkanes and Chloroiodoalkane. Several examples are given below.

1-Acetoxy-1-chloro-2-bromoethane. Vinyl acetate (8.6 g, 100 mmol) was added drop by drop to a mixture of $SbCl_5$ (7.5 g, 25 mmol) and Br_2 (4.0 g, 25 mmol) in CCl_4 (100 ml) near 5 °C. Stirring was continued for 10 min at that temperature, after which the reaction mixture was worked-up as has been described above. Distillation gave the chlorobromide (8.0 g, 39.4 mmol) in a 79% yield; bp 64—65 °C/10 mmHg. NMR: τ 3.45 (t, 1H), 6.25 (d, 2H), 7.84 (s, 3H).

Found: C, 23.90; H, 3.01; Br, 39.30; Cl, 17.43%. Calcd for $C_4H_6BrClO_2$: C, 23.85; H, 3.00; Br, 39.66; Cl, 17.59%.

Diethyl erythro- *and* threo-*α-Bromo-β-chlorosuccinate.* The procedure was the same as that described for vinyl acetate except that the reaction temperature and time were 76 °C and 60 min respectively. From diethyl fumarate (8.6 g, 50 mmol), the *erythro* isomer of diethyl α-bromo-β-chlorosuccinate was obtained in a 66% yield (based on $SbCl_5$ used); bp 121—122 °C/6 mmHg. NMR: τ 5.30—5.40 (m, 2H), 5.72 (q, J=7.5 Hz, 4H), 8.69 (t, J=7.5 Hz, 6H).

Found: C, 33.09; H, 4.08; Br, 28.12; Cl, 12.47%. Calcd for $C_8H_{12}BrClO_4$: C, 33.42; H, 4.21; Br, 27.79; Cl, 12.33%.

In addition, when this ester (5.0 g, 17.4 mmol) was treated with Zn (10.0 g, 154 mmol) (a reagent for specific *trans*-dehalogenation) in boiling ethanol for 5 hr, only the original fumarate was formed as a product (70%).

In a similar way, the *threo* ester was obtained from diethyl maleate in a 52% yield; bp 123—124 °C/9 mmHg. NMR: τ 5.30 (s, 2H), 5.75 (q, J=7.5 Hz, 4H), 8.70 (t, J=7.5 Hz, 6H).

Found: C, 33.73; H, 4.28; Br, 27.54; Cl, 12.20%. Calcd for $C_8H_{12}BrClO_4$: C, 33.42; H, 4.21; Br, 27.79; Cl, 12.33%.

1-Chloro-1-phenyl-2-bromoethane. To a stirred solution of $SbCl_3$ (11.4 g, 50 mmol) and Br_2 (8.0 g, 50 mmol) in CCl_4 (200 ml), styrene (10.4 g, 100 mmol) was added, drop by drop so that the temperature remained near 0 °C. After stirring had been continued for an additional 10 min, the reaction mixture was worked-up as before. Distillation afforded the chlorobromide (9.6 g, 43.7 mmol) in an 87% yield; bp 85—86 °C/2 mmHg (lit,[4] 95—99 °C/3.5 mmHg). The structure was confirmed by a comparison of its IR spectrum with that of an authentic sample prepared from styrene, *N*-bromoacetamide, and HCl.[4]

1,2-Dibromo-3-chloropropane (1) and 1,3-Dibromo-2-chloropropane (2). When allyl bromide (12.1 g, 100 mmol) was treated similarly with a CCl_4 solution (100 ml) containing $SbCl_3$ and Br_2 at the refluxing temperature, a mixture of two isomeric dibromomonochloropropanes (**1** and **2**) was obtained in an 83% yield; bp 94—97 °C/26 mmHg. IR: 725 (s), 650 (m), 627 (m), 610 (m), 568 cm^{-1} (s). The ratio of **1** and **2** was determined by comparisons of the IR spectrum with those of mixtures of a known composition; it was found to be *ca.* 7 : 3. Here, an authentic sample of **1** was prepared from allyl chloride and bromine (bp 84.5—85 °C/18 mmHg [IR: 725 (s), 650 (m), 568 cm^{-1} (s)]), while the authentic sample of **2** was prepared by the chlorination of 1,3-dibromopropan-2-ol with PCl_5 (bp 84—85 °C/18 mmHg [IR: 722 (m), 623 (s), 609 (s), 568 cm^{-1} (m)]).

Some physical data on the other chlorobromide, which was a new compound are given below.

erythro-*1-Carboethoxy-1-bromo-2-chloro-2-phenylethane.* Bp 116—117 °C/11 mmHg. NMR: τ 2.63 (s, 5H), 4.22 (d, 1H), 5.38 (d, 1H), 5.67 (q, 2H), 8.66 (t, 3H).

Found: C, 45.61; H, 4.12; Br, 27.19; Cl, 12.06%. Calcd for $C_{11}H_{12}BrClO_2$: C, 45.31; H, 4.15; Br, 27.40; Cl, 12.16%.

trans-*1-Chloro-2-iodocyclohexane.* To a boiling CCl_4 solution (200 ml) containing $SbCl_5$ (7.5 g, 25 mmol) and I_2 (6.3 g, 25 mmol), cyclohexene (8.2 g, 100 mmol) was added gradually. After stirring had been continued for an additional 10 min, the reaction mixture was worked-up as before with water. The yield of the chloroiodide (11.5 g, 47.0 mmol) was 94%; bp 49—50 °C/1 mmHg (lit,[2a] 37 °C/0.2 mmHg).

References

1) A brief summary is included in Ref. 2a.

2) (a) W. C. Baird, Jr., J. H. Surridge, and M. Buza, *J. Org. Chem.*, **36**, 2088 (1971). (b) W. C. Baird, Jr., J. H. Surridge, and M. Buza, *ibid.*, **36**, 3324 (1971).

3) *E.g.*, R. E. Buckles, J. L. Forrester, R. L. Burham, and T. W. McGee, *ibid.*, **25**, 24 (1960).

4) R. E. Buckles and J. W. Long, *J. Amer. Chem. Soc.*, **73**, 998 (1951).

5) "Handbook of Chemistry and Physics", 39th ed., ed. by C. D. Hodgman, Chemical Rubber Pub. Co., Cleveland, Ohio (1957—58), p. 1637.

6) The known mixed pentahalides of antimony are limited to only a few chlorofluorides ($SbCl_3F_2$, $SbCl_2F_3$, and $SbCl_4F$). Further, considerable thermal stabilities of SbF_5 and $SbCl_5$ are known, but the existence of $SbBr_5$ is unknown. See F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed., Interscience, London (1972), p. 376 and 377.

7) A. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", vol. 9, Longsman, London (1929), p. 487.

8) S. Uemura, A. Onoe, and M. Okano, This Bulletin, in press.

9) S. Uemura, A. Onoe, and M. Okano, This Bulletin, **47**, 147 (1974).

10) (a) M. Baaz, V. Gutmann, and J. R. Msaaguer, *Monatsh. Chem.*, **92**, 582, 590 (1961). (b) Ref. 6, p. 375.

11) A similar ICl formation from $SbCl_5$ and KI was already reported (see Ref. 7, p. 488).

12) E. P. White and P. W. Robertson, *J. Chem. Soc.*, **1939**, 1509.

13) P. B. D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems", Elsevier, Amsterdam (1966), p. 94.

14) H. W. van Dort and Th. J. Sekuur, *Tetrahedron Lett.*, **1963**, 1301.