Selective *cis*-Chlorination of Olefins by Antimony(V) Chloride

By Sakae Uemura,* Osamu Sasaki, and Masaya Okano

(*Institute for Chemical Research, Kyoto University, Uji, Kyoto, Japan*)

Summary Treatment of olefins with $SbCl_5$ in CCl_4 gave *cis-vic*-dichloroalkanes predominantly; *e.g. cis*- and *trans*-but-2-enes and cyclohexene gave *meso*- and (±)-2,3-dichlorobutanes and *cis*-1,2-dichlorocyclohexane respectively.

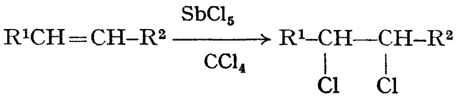
A number of studies of reactions of aromatic compounds with Lewis acid halides of metals and metalloids[1] have been reported, but, except for $CuCl_2$ little is known on the reaction of olefins with these halides. Liquid-phase chlorination of olefins using $CuCl_2$ to give *vic*-dichloroalkanes has been reported recently;[2–4] *cis*- or *trans*-but-2-ene gave a mixture of *meso*- and (±)-2,3-dichlorobutanes, the ratio of *meso* to (±) being almost the same (6:4) for both butenes.[4] A study of the chlorination of olefins with metal or metalloidal chlorides showed that $SbCl_5$ was a good chlorine carrier and reacted smoothly with olefins in CCl_4 to give *cis-vic*-dichloroalkanes predominantly.

The reaction was attempted with *cis*- and *trans*-but-2-ene, oct-1-ene, oct-2-ene, and cyclohexene (Table 1). Organic products were identified by g.l.c. or n.m.r. spectroscopy.

Table 1[a]

Olefins (100 mmol)	$SbCl_5$[b] (in mmol)	Reaction temp. (in °C)	Reaction time (in min)	Product (I) (in mmol)
cis-But-2-ene[c]	23	78	40	10·3[d]
trans-But-2-ene[c]	23	78	40	21·6[e]
Oct-1-ene	25	30	10	16·4
Oct-2-ene[f]	25	30	10	18·4[g]
Cyclohexene	25	78	120	13·4[h]

[a] No attempt was made to optimise the yields. [b] In CCl_4 (100 ml). [c] Olefin gas was introduced to the $SbCl_5$–CCl_4 mixture in a glass reaction vessel. [d] *meso*/(±) = 4·32; pure *meso*- and (±)-isomers were prepared[8] for comparison. [e] (±)/*meso* = 4·43. [f] Mixture of *cis*- and *trans*-isomers. [g] A mixture of *erythro*- and *threo*-isomers; 2-chloro-octane (5·7 mmol) also obtained. [h] *cis*/*trans* = 4·36; chlorocyclohexane (6·0 mmol) also obtained.



(I)

$$R^1CH{=}CH{-}R^2 \xrightarrow[CCl_4]{SbCl_5} R^1{-}\underset{\overset{|}{Cl}}{CH}{-}\underset{\overset{|}{Cl}}{CH}{-}R^2$$

TABLE 2[a]

Metal chlorides (25 mmol)	Reaction temp. (in °C)	Reaction time (in h)	Products (in mmol)			
			(II)	(III)	(IV)	(IV)/(III)
$SbCl_5$	78	0·083	4·4	2·8	13·9	4·96
$SbCl_5$	30	0·05	5·5	7·2	14·9	2·07
$SbCl_5$	30	0·083	6·5	10·7	15·7	1·47
$SbCl_5$[b]	30	0·083	3·6	8·1	8·6	1·06
$TlCl_3,4H_2O$	78	2	13·7	4·3	0·1	0·027
$CuCl_2,2H_2O$[c]	100	13	0	14·4	0·2	0·016
$CuCl_2$[d]	77	18	0	14·6	0·3	0·022
$FeCl_3$	78	2	7·7	trace	trace	—

[a] Cyclohexene (100 mmol); CCl_4 (100 ml). [b] Solution of $SbCl_5$ in CCl_4 was added. [c] Cu salt (150 mmol), AcOH solvent (100 ml) NaOAc (100 mmol) was added. [d] Cu salt (100 mmol), MeCN solvent (100 ml), LiCl (100 mmol) was added.

The data for *cis*- and *trans*-but-2-enes and cyclohexene show that this chlorination proceeds mainly in *cis* fashion.

From the synthetic point of view more detailed studies were carried out with cyclohexene. Chlorocyclohexane (II), *trans*-1,2-dichlorocyclohexane (III) and the *cis*-isomer (IV) were the only organic products. Data are shown in Table 2, with results for other metal chlorides for comparison. All reactions except one were carried out by addition of cyclohexene to metal chloride-solvent mixture. The chlorination with $SbCl_5$ is exothermic, and was complete in 5 min at room temperature in CCl_4, but it did not occur in solvents such as MeCN or $MeNO_2$. In $MeNO_2$ slight oxidation to cyclohexanone was observed. With CCl_4 under reflux, (IV) was formed preferentially; blank experiments eliminated the possibility of interconversion of (III) and (IV). Addition of $SbCl_5$ to a mixture of cyclohexene and CCl_4 gave almost equal amounts of (III) and (IV) at 30°. The chlorination with $TlCl_3,4H_2O$, $CuCl_2,2H_2O$ or $CuCl_2$ in a suitable solvent gave (III) almost entirely as in the usual chlorination with chlorine gas.[5,6] $FeCl_3,6H_2O$, $SbCl_3$, and $CuCl_2$ gave no chlorinated products in CCl_4.

Since (IV) can be separated from (II) and (III) by distillation [b.p. 63° at 9 Torr; τ 5·6—5·7 (m, 2H), 8·05 (m, 4H), and 8·3 (m, 4H)] this method of synthesis has advantages over literature methods which involve many steps.[5,7]

Although the reason for the favourable *cis*-addition is not clear, five-centred molecular addition of chlorine to the olefin involving Sb participation might be involved in the transition state.

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