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The Chlorination of Norbornene by Metal Chlorides and the Product Isomerization

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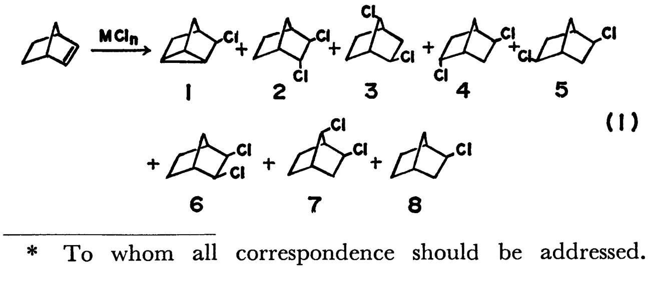
The reaction of norbornene with $CuCl_2$, $TlCl_3 \cdot 4H_2O$, $PbCl_4$, $SeCl_4$, $SbCl_5$, and VCl_4 in CCl_4, CH_2Cl_2, or CH_3CN gave a mixture of nortricyclyl chloride (**1**), and six isomeric dichloronorbornanes [*trans*-2,3-(**2**), *exo*-2-*anti*-7-(**3**), *trans*-2,5-(**4**), *exo*-*cis*-2,5-(**5**), *exo*-*cis*-2,3-(**6**), and *exo*-2-*syn*-7-(**7**)], the product distribution depending very much on metal chlorides and reaction conditions. The reactions did not show any participation of a chlorine molecule which may be released from metal chlorides. The ability of $SeCl_4$ and VCl_4 to chlorinate olefins was found for the first time. From a synthetic viewpoint $CuCl_2$ was a good reagent for obtaining **2**, while $TlCl_3 \cdot 4H_2O$ and $SbCl_5$ were recommended for either **3** or **7**. The reactions with the following metal chlorides did not give any dichloronorbornanes; $SnCl_4$, $BiCl_3$, $TiCl_4$, $FeCl_3$, $NbCl_5$, $TaCl_5$, and WCl_6. It was revealed that isomerization of **2** or **7** to a mixture of **3**, **4**, and **5** occurred very rapidly by $SbCl_5$ and smoothly by $TlCl_3 \cdot 4H_2O$. The chlorination of norbornene and their products isomerization were mainly explained by assuming a chloronorbornyl cation as an intermediate.

Recently we have shown that the chlorination of norbornene by $SbCl_5$[1)] and $MoCl_5$[2)] gave a quite different distribution of the products with that by Cl_2[3)] and (dichloroiodo)benzene.[4)] Namely, *exo*-2-*anti*-7-(**3**), *trans*-2,5-(**4**), and *exo*-*cis*-2,5-dichloronorbornane(**5**) were the main products in the case of $SbCl_5$, while *exo*-*cis*-2,3-isomer(**6**) was mainly obtained in the case of $MoCl_5$. On the other hand, a mixture of nortricyclyl chloride(**1**) and *exo*-2-*syn*-7-isomer(**7**) (ionic condition) and a mixture of *trans*-2,3-iosmer(**2**) and **6** (radical condition) were mainly obtained in chlorination by Cl_2 or $PhICl_2$. In the chlorination of olefin by metal chloride it is sometimes difficult to distinguish whether it is a specific reaction by metal chloride itself or it involves a chlorine molecule released from metal chloride. The clear-cut different product distribution described above, however, suggests that norbornene is a good olefinic substrate to study whether the reaction involves a chlorine molecule. Therefore we carried out its chlorination by various metal chlorides with the intentions of giving a further insight on the nature of metal chloride chlorination and also of finding any metal chlorides for selective formation of each of **1**–**7** if possible.

Results and Discussion

Reaction conditions, the yields of the products, and the isomer distributions are summarized in Table together with the reported data of $MoCl_5$[2)] and $AuCl_3$[5)] (Scheme 1). The data of typical ionic and radical chlorination by Cl_2[3)] were also added for comparison. All reactions were carried out by addition of norbornene to a solution of metal chloride in the presence of atomospheric amounts of oxygen unless otherwise stated.



CuCl₂. The reaction proceeded smoothly in CH_3CN where LiCl was added to increase the reaction rate and the solubility of copper(II) salt to give **2** and **6** almost selectively (Run 1), while no reaction occurred in CCl_4, CH_2Cl_2, and $CHCl_3$ as solvents. Although the isomer distribution in the products, which was shown to be kinetically controlled one, was similar to that in radical chlorination by Cl_2[3)] or $PhICl_2$,[4)] the reaction was not affected by addition of *m*-dinitrobenzene (Run 2) and no change in the product distribution was observed even when the reactions were conducted under bubbling oxygen or nitrogen. Therefore it is clear that the chlorinating species is not a chlorine molecule which may be released from $CuCl_2$, but $CuCl_2$ itself or its LiCl complex.

TlCl₃·4H₂O. Chlorination by this salt in CCl_4 at refluxing temperature afforded a mixture of **3**, **4**, **5**, and **7**, the ratio of a mixture of **3**—**5** to **7** being increased by prolonging the reaction time (Runs 3 and 4). The reaction proceeded even at −10 °C where the compounds other than **3** and **7** were scarcely obtained (Run 5). We showed in separate experiments that **7** isomerized smoothly to a mixture of **3**—**5** in CCl_4 at 5—76 °C in the presence of $TlCl_3 \cdot 4H_2O$, while no isomerization occurred at −10 °C (See Experimental). Therefore it can be concluded that the isomer distribution in Run 5 is kinetically controlled. The formation of *exo*-2-chloronorbornane(**8**), HCl addition product to norbornene, was observed in Runs 3 and 4. The evolution of HCl by interaction of $TlCl_3 \cdot 4H_2O$ with CCl_4 at refluxing temperature has been known.[6)]

PbCl₄. Chlorination by this salt was carried out by addition of olefin to a yellow CH_2Cl_2 solution of $PbCl_4$[7)] which was produced *in situ* by action of HCl on $Pb(OAc)_4$ at −60 °C. The characteristic feature of this reaction was found in selective formation of **3** and **7** without any other isomers when the reaction was conducted at −40 °C (Run 6). It was shown in separate experiments that neither interconversion between **3** and **7** nor isomerization of other isomers to **3** and **7** occurred in CH_2Cl_2 at −30—−40 °C in the presence of $PbCl_4$ and/or $PbCl_2$. Therefore the isomer distribution in Run 6 is kinetically cotnrolled. The reaction also proceeded in CCl_4 at −10 °C (Run 7),

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though the formation of **1** was observed in this case probably because of the slight release of a chlorine molecule from $PbCl_4$ at this temperature. Since excess HCl is present in solution, **8** was always formed as a side-product.

$SbCl_5$. We have reported previously that the chlorination of norbornene by this chloride in CCl_4 gave mainly **3**, **4**, and **5** in good yields.[1] In view of the observation that **7** was isomerized to a mixture of **3**—**5** by $TlCl_3 \cdot 4H_2O$, we reexamined the product distributions under various conditions. When norbornene was added drop by drop in a period of *ca.* 0.5—3 min to a CCl_4 solution of $SbCl_5$ (Run 8), none of **7** was obtained and the main products were **3**—**5** as shown in our previous report.[1] However, when norbornene was added all at once (Runs 9—11), **3** and **7** were obtained as the main products, while the amounts of **4** and **5** in the products were very small. In these cases the product distribution appeared to be nearly constant irrespective of the total reaction time and its temperature. When the reverse addition was employed (Run 12), namely addition of a CCl_4 solution of $SbCl_5$ to a CCl_4 solution of norbornene, the product distribution was nearly the same as those in Runs 9—11 almost irrespective of the speed of the addition. In separate experiments we observed that $SbCl_5$ was a very effective catalyst for isomerization of **2** and **7** to a mixture of **3**—**5**, while $SbCl_3$ showed no effectiveness for such isomerization. For example, almost all of **2** or **7** were converted to a mixture of **3**—**5** by treating with $SbCl_5$ at 20 °C in only 10 min (See Experimental). The chlorination of norbornene by $SbCl_5$ occurs very rapidly under the conditions we employed and it was nearly complete as soon as norbornene was added to a solution of $SbCl_5$ (Run 9). Thus we can conclude that in Run 8 initially formed **7** was isomerized to a mixture of **3**—**5** by excess $SbCl_5$ present in a solution, while in Runs 9—11 and also in Run 12 $SbCl_5$ did not exist in such extent as making the isomerization of **7** complete, because $SbCl_5$ turned to $SbCl_3$ as soon as chlorination took place. Since there have been no convenient methods of preparing **4** and **5**, the method described here (Run 8) seems to be useful for this purpose.

$SeCl_4$ and VCl_4. We have tried to chlorinate norbornene by several other commercial metal chlorides with which chlorination of olefin has never been reported. As a result both $SeCl_4$ and VCl_4 were revealed to chlorinate olefins. The following metal chlorides did not give any dichloroalkanes under the conditions we have employed (cyclohexene and norbornene as substrates; at 20—76 °C in CCl_4); $SnCl_4$, $BiCl_3$, $TiCl_4$, $FeCl_3$, $NbCl_5$, $TaCl_5$, and WCl_6.

As to chlorination by $SeCl_4$, there have been no reports on direct chlorination of olefins, although the reaction of $SeCl_4$ with unsaturated linkages to produce organoselenium dichlorides has been well known.[8] However, chlorination occurred with norbornene in CCl_4 to give several dichloronorbornanes in which **7** was the main product (Runs 13 and 14). Since we

TABLE. CHLORINATION OF NORBORNENE

Run	Norbornene (mmol)	Chlorinating agent	(mmol)	Solvent (50 ml)	React. Temp. (°C)	React. Time (hr)	Addendum (mmol)	Products								By-product **8** (mmol)
								Isomer distribution							Yield[a] (%)	
								1	**2**	**3**	**4**	**5**	**6**	**7**		
1	12.5	$CuCl_2$	25	CH_3CN	82	3	LiCl 25	0	80	0	0	0	18	2	90	
2	12.5	$CuCl_2$	25	CH_3CN	82	3	LiCl 25 *m*-DNB[b] 5	0	82	0	0	0	15	3	87	
3	12.5	$TlCl_34H_2O$	6.3	CCl_4	76	0.1		s.[c]	2	34	5	5	0	54	23	0.7
4	12.5	$TlCl_34H_2O$	6.3	CCl_4	76	2		s.	2	45	11	10	0	32	62	3.1
5	12.5	$TlCl_34H_2O$	6.3	CCl_4	−10	3		s.	1	31	1	1	0	66	48	
6	11	$PbCl_4$	5	CH_2Cl_2	−40	3		0	0	41	0	0	0	59	57	7.8
7	11	$PbCl_4$	5	CCl_4	−10	2		30	0	13	0	0	0	57	58	0.7
8	5	$SbCl_5$	3	CCl_4[d]	20	0.17[e]		0	3	35	31	31	0	0	81	
9	5	$SbCl_5$	3	CCl_4[d]	20	5 sec[f]		0	1	52	9	7	0	31	84	
10	5	$SbCl_5$	3	CCl_4[d]	20	0.17[f]		0	s.	50	7	6	0	37	91	
11	5	$SbCl_5$	3	CCl_4[d]	−30	0.17[f]		0	s.	52	6	6	0	36	91	
12	5	$SbCl_5$	3	CCl_4[d]	20	0.17[g]		0	1	49	3	2	0	45	85	
13	5	$SeCl_4$	3	CCl_4	76	2		0	s.	20	2	3	0	75	31	
14	5	$SeCl_4$	3	CCl_4	25	12		0	s.	22	3	2	0	73	22	
15	20	VCl_4	7	CCl_4	76	2		4	11	7	6	4	64	4	67	1.7
16	5	VCl_4	3.5	CCl_4	27	12		1	14	5	1	s.	71	8	32	0.3
17[h]	4	$MoCl_5$	1.3	CCl_4	25	2		0	1	7	13	11	68	0	42	0.7
18[i]	6—15	$AuCl_3$	3—5	C_6H_{12}[j]	20	—[k]		0	0	←—66—→			0	34	77	
19	—[k]	Cl_2	—[k]	CCl_4	25	0.5	O_2	65	6	0	0	0	4	25	95	
20	—[k]	Cl_2	—[k]	CCl_4	25	0.5	N_2, hν	19	37	0	0	0	35	0	—[k,l]	

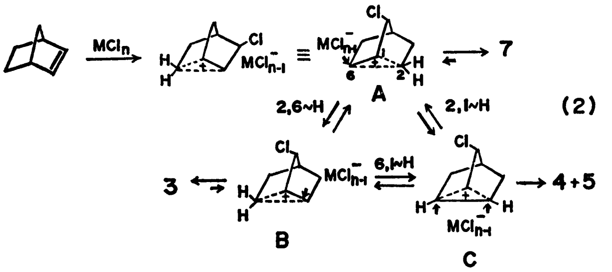
a) Based on MCl_n charged. Determined by glc. b) *m*-Dinitrobenzene. c) $<0.5\%$. d) 10 ml. e) Olefin was added in *ca.* 20—30 sec. f) Olefin was added all at once. g) $SbCl_5$ was added to olefin. h) Ref. 2. i) Ref. 5. j) Cyclohexane. k) No description. l) Other products; *exo-* and *endo*-5-chloro-2-norbornenes, 6% and 3% respectively.

showed in separate experiments that **7** did not isomerize to other isomers under the reaction conditions, the isomer ratios in Runs 13 and 14 seem to be kinetically controlled. The reaction of cyclohexene with $SeCl_4$ gave *trans*-dichlorocyclohexane in a 44% yield together with chlorocyclohexane by stirring at 20 °C for 2 hr. In order to see whether these dichloroalkanes were produced *via* organoselenium compounds, we prepared separately bis(2-chlorocyclohexyl)selenium dichloride by the reported method[8] (mp 142 °C; lit,[8] mp 141—142 °C) and heated it to reflux in CCl_4 for 2 hr in the presence or absence of $SeCl_4$. As a result none of dichlorocyclohexane was obtained. This shows that chlorination by $SeCl_4$ does not proceed through the formation of organoselenium compounds at least in CCl_4 solvent.

The chlorination of norbornene by VCl_4 proceeded smoothly in CCl_4 to give all of **1**—**7** in which the main product was the *cis*-dichlorinated isomer **6** (Runs 15 and 16). Although the chlorinating action of VCl_4 has been noted in the chlorination of aromatic hydrocarbons,[9] there have so far been no reports on the direct chlorination of olefins. Since we showed that no isomerization occurred between each isomer under the conditions of Runs 15 and 16 and also that the isomer distribution was nearly the same even when the reaction was stopped in a shorter time, the isomer ratios shown in Table are clearly kinetically controlled. Although a preferential formation of **6** is quite charactistic, chlorination of norbornadiene and cyclohexene gave hardly any *cis*-dichloroalkanes. Therefore, the molecular *cis*-addition mechanism which was proposed in the chlorination by $MoCl_5$[2] does not seem to be applicable in this case. It should be added that radical scheme can be excluded because no change in the isomer distribution and the yields of the products was observed when the reactions were conducted under the presence of *m*-dinitrobenzene or bubbling oxygen.

By considering the product distribution in each reaction described above, we can conclude that chlorination by any metal chlorides does not involve a chlorine molecule which may be released from metal chlorides. Since a fractional distillation can nearly separate **2** from **6** and also **3** from **7**, additional useful conclusion can be drawn from a synthetic viewpoint. For obtaining **2** chlorination by $CuCl_2$ (Run 1) is recommended, while for either **3** or **7** the reactions with $TlCl_3\cdot 4H_2O$ (Run 5) and $SbCl_5$ (Run 12) should be employed because of its simplicity, high selectivity, and high yields of the products. In order to obtain **4** and **5**, the method of Run 8 by the use of $SbCl_5$ is applicable, though it is necessary to use preparative glc for the separation of each isomer.

Reaction Scheme and Product Isomerization. The results that chlorinations by $TlCl_3\cdot 4H_2O$, $PbCl_4$, $SbCl_5$, and $SeCl_4$ gave mainly **3** and **7** as kinetically controlled products (usually **7**>**3**) seem to be explained by Scheme 2. Namely, at first a chloronorbornyl cation **A** may be formed as an intimate ion-pair with gegen-ion MCl_{n-1}^- because of low polarity of solvent. In some extent the cation may be converted to another isomeric bridged ion **B** through 2,6-hydride shift. As noted earlier,[10] the low cationic character at C_1 in **A** and **B** due to the inductive effect of the adjacent chlorine atom probably prevents the attack of MCl_{n-1}^- on C_1, and makes the almost exclusive attack on C_6 and C_2 possible, leading to the formation of **7** and **3** respectively. It is also apparent by similar reason that 6,1- or 2,1-hydride shift to give **C** would be less important than 2,6-shift, and hence **4** and **5** are minor products. Such equilibrium as shown in Scheme 2 has been assumed to explain the result of the acetolysis and isomerization of *syn*- and *anti*-7-chloro-*exo*-norbornyl *p*-toluenesulfonate.[11]



(2)

In the chlorination by VCl_4, the reaction scheme for the formation of **2** and **6** is not yet clear. The isomer distribution in the minor products, however, suggests that the reaction proceeded through Scheme 2 to some extent.

Chlorination by $CuCl_2$ which gave 2,3-dichloronorbornanes almost selectively and only a small amount of carbon skeleton rearranged product, on the contrary, does not seem to proceed through Scheme 2. Coordination of copper salt on double bond may be one of the determining factors for such selective formation.

Isomerization of **2** or **7** to a mixture of **3**—**5** by rather strong Lewis acids such as $SbCl_5$ and $TlCl_3\cdot 4H_2O$ in CCl_4 may be explained by Scheme 2. Thus, the abstraction of *exo*-Cl (on C_2) by MCl_n gives the cations **A** and **B** from **7** and **2** respectively which then afford **3**—**5** by recombination with Cl^- of MCl_{n+1}^-. We also observed the slow isomerization of **3** to **4** and **5** by $SbCl_5$ and $TlCl_3\cdot 4H_2O$ at 20 °C and 76 °C respectively. This isomerization may involve the abstraction of *exo*-Cl from **3**. It should also be noted that no isomerization of **6** by $SbCl_5$ was observed at 20 °C for 10 min in CCl_4. The reason why **6** is so stable compared to **2** is not yet clear.

Experimental

All materials except $PbCl_4$[7] were commercial products and used without further purification. The identification of each product was described in previous papers.[1,2] The product distributions were analyzed by glc by the use of Shimadzu apparatus 5APTF and 4BMPF on both EGSS-X(15%)-Chromosorb-W (3 m) and PEG 6000 (25%)-Chromosorb-W (3 m) columns (carrier gas, N_2; bromobenzene or *trans*-dichlorocyclohexane as internal standard). In the reaction with VCl_4 or $SeCl_4$, **6** or **7** was isolated respectively by a fractional distillation in almost pure state and analyzed by NMR to ascertain the structure (Varian A-60 spectrometer; in CCl_4).

Synthesis of **2**. A homogeneous mixture of $CuCl_2$ (26.8 g, 200 mmol), LiCl (8.4 g, 200 mmol), CH_3CN (200 ml) and norbornene (4.7 g, 50 mmol) was stirred for 5 hr under reflux. After being cooled down to room temperature the mixture was concentrated to *ca.* 50 ml by evaporation of solvent, added by water (300 ml), and then extracted with benzene. Distillation of the extract through a fractionating column (30 cm) with glass packings afforded two fractions leaving only a small amount of residue; D_1 5.0 g (bp 89—94 °C/19 mmHg) and D_2 0.86 g (bp 88—92 °C/10 mmHg). The fraction D_1 was shown by glc to contain **2** (95%) and small amounts of **6** and **7**. The fraction D_2 was revealed to be a mixture of **2**(15%), **6**(75%), and **7**(10%).

*Synthesis of **3** and **7**.* To a CCl_4 (170 ml) solution of norbornene (4.7 g, 50 mmol) was slowly added a yellow homogeneous CCl_4 (30 ml) solution of $SbCl_5$ (10.0 g, 33.4 mmol) at 20 °C for 5 min. After 5 min, water was added to the reaction mixture and the precipitated SbOCl was filtered off. Similar fractional distillation of the filtrate as described above afforded three fractions; D_1 2.1 g (bp 95—98 °C/18 mmHg), D_2 1.2 g (bp 102—109 °C/18 mmHg), and D_3 0.43 g (bp 75—77 °C/5 mmHg). The fraction D_1 was shown by glc to contain **3**(90%) and small amounts of **2**, **4**, **5**, and **7**. The fraction D_3 was shown to be a mixture of **3**(13%), **7**(84%) and small amounts of **4** and **5**.

*Isomerization of **7** or **2** to a Mixture of **3**—**5** by $TlCl_3 \cdot 4H_2O$.* A CCl_4 (25 ml) solution containing **7** (0.22 g, 1.33 mmol) and $TlCl_3 \cdot 4H_2O$ (0.80 g, 2.09 mmol) was stirred at 76 °C for 2 hr. After being cooled down to room temperature, organic layer was washed with water and analyzed by glc. The products were **2**(3.6%), **3**(27.6%), **4**(28.8%), **5**(34.6%), and **7**(5.4%); recovered yield of dichloronorbornanes was 90%. Similar treatment of **7** at 5 °C for 3 hr gave a mixture of **2**(0.4%), **3**(39.4%), **4**(19.8%), **5**(1.6%), and **7**(38.8%); yield, 91%. When **2**(1.04 mmol) was stirred in CCl_4 (25 ml) with $TlCl_3 \cdot 4H_2O$ (1.68 mmol) at 76 °C for 2 hr, it isomerized to a mixture of **2**(6.9%), **3**(21.3%), **4**(36.6%), and **5**(35.2%); yield, 89%. No isomerization of **2** or **7** to other isomers was observed at −10 °C.

*Isomerization of **7** or **2** to a Mixture of **3**—**5** by $SbCl_5$.* A CCl_4 (25 ml) solution containing **7** (1.47 mmol) and $SbCl_5$ (1.67 mmol) was kept at 20 °C for 10 min. Glc analysis of CCl_4 layer after usual work-up procedure revealed the presence of a mixture of **2**(5.4%), **3**(40.7%), **4**(24.3%), **5**(29.4%), and **7**(0.2%); yield of a mixture, 96%. Similar treatment of **2**(1.12 mmol) with $SbCl_5$ (1.69 mmol) gave a mixture of **2**(4.2%). **3**(17.6%), **4**(36.3%), and **5**(41.9%); yield, 98%.

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