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The Chlorination of Norbornadiene by Various Chlorinating Agents

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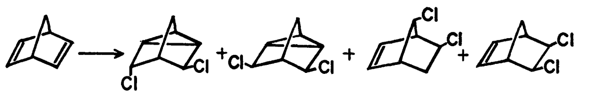
Synopsis. The chlorination of norbornadiene by $CuCl_2$, $TlCl_3 \cdot 4H_2O$, $SbCl_5$, $SeCl_4$, and VCl_4 in CCl_4 or CH_3CN afforded mainly *trans*-3,5-(**1**) and *exo-cis*-3,5-dichloronortricyclene (**2**). In the reaction with $PbCl_4$, Cl_2, SO_2Cl_2, and PCl_5, appreciable amounts of *exo*-5-*syn*-7-(**3**) and/or *exo-cis*-5,6-dichloronorbornene (**4**) were obtained besides **1** and **2**.

Concerning the chlorination of norbornadiene, the reactions with $CuCl_2$ (gas-phase),[1] Cl_2,[2] $PhICl_2$,[2] $AuCl_3$,[3] and $MoCl_5$[4] have so far been reported. We now give the results of chlorination by various other chlorinating agents. Among the chlorinating agents examined the following were found to be effective: $CuCl_2$, $TlCl_3 \cdot 4H_2O$, $SbCl_5$, $SeCl_4$, VCl_4, $PbCl_4$, SO_2Cl_2, and PCl_5. The products were two isomeric dichloronortricyclenes [*trans*-3,5-(**1**) and *exo-cis*-3,5-(**2**)] and two isomeric dichloronorbornenes [*exo*-5-*syn*-7-(**3**) *exo-cis*-5,6-(**4**)], the distribution of the products depending a great deal on the kind of chlorinating agent and the reaction conditions. The results are shown in the Table together with our previous data on $MoCl_5$.[4]



1 **2** **3** **4**

The product distribution suggests that the chlorinating agents can be classified for convenience into three categories. The first class consists of $CuCl_2$, $TlCl_3 \cdot 4H_2O$, $SbCl_5$, $SeCl_4$, and VCl_4, which gave almost entirely **1** and **2**. Although a radical mechanism has been proposed for the formation of **1** and **2** by $PhICl_2$,[2] it was found that the reactions by these metal chlorides were ionic since no effect was observed by the addition of radical scavengers such as *m*-dinitrobenzene (*m*-DNB) and oxygen, or even when the reactions were carried out under N_2. Furthermore we have observed that the reaction of other olefins such as cyclohexene[5] and norbornene[6] with these metal chlorides proceeds by an ionic mechanism under nearly the same reaction contions. The ability of $SeCl_4$ and VCl_4 to chlorinate olefin, which was firstly found in the reaction with norbornene,[6] was also confirmed in this case (Runs 4 and 5), but no favorable *exo-cis*-addition by VCl_4 as observed in the case of norbornene[6] was found (Run 5).

The second class consists of $PbCl_4$, Cl_2, SO_2Cl_2, and PCl_5, which generally afforded a mixture of **1**, **2**, and **3**. The reactions with SO_2Cl_2 and PCl_5 at higher temperature gave **4** as an additional product (Runs 9 and 11). It is evident that at least **4** is formed by a radical pathway,[7] since the addition of *m*-DNB profoundly decreased the total yield of the products, affording none of **4**. In contrast, in the reactions with chlorine (in the dark) the formation of **4** was only slight (Run 7) and *m*-DNB and bubbling oxygen gave no effect on product distribution, suggesting an ionic process. The ionic nature of $PbCl_4$ was previously reported in the chlorination of norbornene.[6]

The mechanism for the formation of **1**—**3** might be essentially the same as that proposed by Winstein[8] in the bromination of norbornadiene. The attack of anion on C_3 and C_1 of a nonclassical chloronorbornyl cation

TABLE CHLORINATION OF NORBORNADIENE

Run	Norbornadiene (mmol)	Chlorinating agent (mmol)	Solvent (50 ml)	React temp (°C)	React time (hr)	Products Isomer distribution (%) **1**	**2**	**3**	**4**	Yield (%)[a]
1	25	$CuCl_2$[b]	25 CH_3CN	80	2	49	50	1	0	82
2	25	$TlCl_3 \cdot 4H_2O$	12.5 CCl_4	76	2	51	49	0	0	86
3	25	$SbCl_5$	12.5 CCl_4	27	0.2	56	41	3	0	80
4	25	$SeCl_4$	2.8 CCl_4	76	12	40	55	5	0	28
5	20	VCl_4	3 CCl_4	76	2	64	33	1	2	38[c]
6	25	$PbCl_4$	5 CH_2Cl_2	−40	2	49	22	29	0	78[d]
7	25	Cl_2	70 CCl_4	−20	2	40	14	43	3	91
8	50	SO_2Cl_2	25 CCl_4	20	20	63	25	12	0	36
9	50	SO_2Cl_2	25 CCl_4	76	2	39	18	29	14	95
10	50	PCl_5	25 CH_2Cl_2	40	5	46	24	29	1	89
11	25	PCl_5	12.5 CCl_4	76	2	41	41	13	5	58
12[e]	5	$MoCl_5$	2 CCl_4	25	2	22	10	<0.5	68	20

a) Based on the chlorinating agent. Determined by glc. b) LiCl (25 mmol) was added. c) Other products; nortricyclyl chloride (0.2 mmol). d) Other products; nortricyclyl chloride (1.26 mmol) and *exo*-5-chloro-2-norbornene (3.6 mmol). e) Ref. 4.

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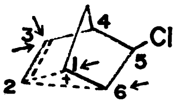
(**A**) gives a mixture of **1** and **2**, and **3**, respectively. However, the reason why only the chlorinating agents in this class give **3** is not yet clear. The attack on C_6, which affords **4**, might be sterically unfavorable.



(**A**)

The last class contains only $MoCl_5$ which gave mainly **4** probably by molecular *cis*-addition mechanism.[4)]

From a synthetic viewpoint chlorination by $SbCl_5$ is recommended for preparation of **1** and **2** because of its simplicity and high yields of the products. For **3** and **4**, the reactions with PCl_5 (in CH_2Cl_2) and $MoCl_5$, respectively, should be employed, though it is necessary to use preparative glc for isolating each isomer in a pure state.

Experimental

All materials except $PbCl_4$ were commercial products and used without further purification. The reactions were usually carried out by mixing all the reagents at room temperature and then keeping the mixture at reaction temperature under the presence of atmospheric oxygen. In the case of VCl_4, a CCl_4 solution of VCl_4 was added to a CCl_4 solution of norbornadiene in order to avoid the polymerization of diene. In the case of Cl_2, chlorine gas was introduced to a CCl_4 solution of norbornadiene at −20 °C. The identification of each product, **1**—**4**, was described previously.[4)] The product mixtures 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).

Reaction with $PbCl_4$. A solution of CH_2Cl_2 (50 ml) containing $Pb(OAc)_4$ (2.22 g, 5.0 mmol) was kept at −60 °C and was introduced by HCl gas for 10 min.[9)] To this solution was slowly added norbornadiene (2.3 g, 25 mmol) at −40 °C and the solution was stirred for 2 hr. After the usual work-up, the organic layer was evaporated to *ca.* 7 ml and analyzed by glc; *exo*-5-chloro-2-norbornene (3.6 mmol), nortricyclyl chloride (1.26 mmol), **1** (1.93 mmol), **2** (0.86 mmol), and **3** (1.13 mmol). The formation of the former two compounds by the reaction of norbornadiene with HCl has been reported.[10)]

Synthesis of 1 and 2. A CCl_4 (50 ml) solution of $SbCl_5$ (15 g, 50 mmol) was added to a CCl_4 (150 ml) solution of norbornadiene (9.2 g, 100 mmol) at 25 °C in *ca.* 1 min and the resulting clear solution was stirred for 10 min. To this solution was added water and the precipitated SbOCl was filtered and then CCl_4 layer was distilled to give 6.5 g (80% yield) of a mixture of **1** and **2** (**1**: **2**=58: 42); bp 95—96 °C/22 mmHg. The NMR spectrum of both **1** and **2** (separated by preparative glc) was identical with the spectra reported.[2,3)]

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