

The Chlorination of Norbornadiene by Various Chlorinating Agents

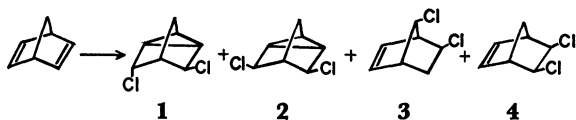
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Synopsis. The chlorination of norbornadiene by CuCl_2 , $\text{TiCl}_3 \cdot 4\text{H}_2\text{O}$, SbCl_5 , SeCl_4 , and VCl_4 in CCl_4 or CH_3CN afforded mainly *trans*-3,5-(**1**) and *exo-cis*-3,5-dichloronorbornene (**2**). In the reaction with 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 , $\text{TiCl}_3 \cdot 4\text{H}_2\text{O}$, SbCl_5 , SeCl_4 , VCl_4 , PbCl_4 , SO_2Cl_2 , and PCl_5 . The products were two isomeric dichloronorbornenes [*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⁾



The product distribution suggests that the chlorinating agents can be classified for convenience into three categories. The first class consists of CuCl_2 , $\text{TiCl}_3 \cdot 4\text{H}_2\text{O}$, 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 cyclohexene⁵⁾ and norbornene⁶⁾ with these metal chlorides proceeds by an ionic mechanism under nearly the same reaction conditions. 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 norbornene⁶⁾ 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 Winstein⁸⁾ in the bromination of norbornadiene. The attack of anion on C_3 and C_1 of a nonclassical chloronorbornyl cation

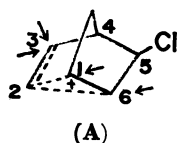
TABLE CHLORINATION OF NORBORNADIENE

Run	Norbornadiene (mmol)	Chlorinating agent (mmol)	Solvent (50 ml)	React temp (°C)	React time (hr)	Products Isomer distribution (%)				Yield (%) ^{a)}
						1	2	3	4	
1	25	CuCl_2 ^{b)}	25 CH_3CN	80	2	49	50	1	0	82
2	25	$\text{TiCl}_3 \cdot 4\text{H}_2\text{O}$	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; norbornene (0.2 mmol). d) Other products; norbornene (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 C₆, which affords **4**, might be sterically unfavorable.



The last class contains only MoCl₅ which gave mainly **4** probably by molecular *cis*-addition mechanism.⁴⁾

From a synthetic viewpoint chlorination by SbCl₅ 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 PCl₅ (in CH₂Cl₂) and MoCl₅, respectively, should be employed, though it is necessary to use preparative glc for isolating each isomer in a pure state.

Experimental

All materials except PbCl₄ 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 VCl₄, a CCl₄ solution of VCl₄ was added to a CCl₄ solution of norbornadiene in order to avoid the polymerization of diene. In the case of Cl₂, chlorine gas was introduced to a CCl₄ 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, N₂; bromobenzene or *trans*-dichlorocyclohexane as internal standard).

Reaction with PbCl₄. A solution of CH₂Cl₂ (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 CCl₄ (50 ml) solution of SbCl₅ (15 g, 50 mmol) was added to a CCl₄ (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 CCl₄ 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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