

Lewis Acid-Catalyzed Rearrangement of 2,2-Dichloronorbornane to 1-Chloronorbornane

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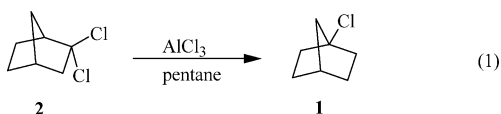
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Received November 14, 2003

Abstract: The mechanism for the unusual AlCl₃-catalyzed rearrangement of 2,2-dichloronorbornane to 1-chloronorbornane in pentane has been elucidated; the reaction, which also yields four isomeric dichloronorbornanes, occurs in three steps: (1) ionization to form the 2-chloro-2-norbornyl cation, which was fully characterized by two-dimensional ¹H and ¹³C NMR in SbF₅/SO₂ClF; (2) Wagner–Meerwein shift to yield the 1-chloro-2-norbornyl cation, which was partially characterized by ¹H NMR; and (3) hydride abstraction.

1-Chloronorbornane (**1**) is an interesting molecule because its geometry precludes it undergoing the S_N2 reaction and inhibits the S_N1 reaction. It is also a source of the 1-norbornyl cation,^{1–3} radical,^{4,5} and anion.^{6,7} It is prepared by the unusual aluminum chloride-catalyzed rearrangement of 2,2-dichloronorbornane (**2**) in pentane (eq 1). Overall, one chlorine appears to change position while the second is replaced by hydrogen. 2,2-Dibromonorbornane reacts similarly, yielding 1-bromonorbornane in AlBr₃/pentane.⁹ How do these remarkable rearrangements occur? What is the source of hydrogen in the product?



The initial steps in the rearrangement of 2,2-dichloronorbornane appear to be ionization to form the 2-chloro-2-norbornyl cation (**3**) followed by a Wagner–Meerwein shift to yield the 1-chloro-2-norbornyl cation (eq 2). To



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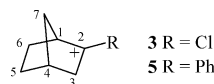
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assess the viability of this conjecture, 2,2-dichloronorbornane was treated with SbF₅ in SO₂ClF at –100 °C. On the basis of the ¹H and ¹³C NMR and correlation (COSY, HMQC, DEPT, NOESY) NMR spectra of the resulting solution at –100 °C, as well as comparison to the ¹H and ¹³C NMR spectra of the 2-phenyl-2-norbornyl cation (**5**),^{2,10,11} the observed species is identified as the 2-chloro-2-norbornyl cation (**3**). See Table 1 for NMR assignments of **3** and **5**.



When the solution containing the 2-chloro-2-norbornyl cation (**3**) was warmed to –20 °C, the ion was converted into a new species which in turn decomposed. However, the new species could be characterized as the 1-chloro-2-norbornyl cation (**4**). The original seven resonances in the proton-decoupled ¹³C NMR spectrum were replaced by seven new ones [5 sharp (284.4, 91.1, 61.3, 42.7, 37.2) and 2 broad (~78, ~41) due to chemical exchange]. The C-2 resonance in the original ion at δ 284.5 was replaced by a new one at δ 284.4, while C-1 in the original ion at δ 76.9 was replaced by a peak at δ 91.1 which is assigned to C₁, the one bonded to chlorine. In the ¹H NMR spectrum of the new ion a resonance appeared at δ 5.6 which is consistent with H₂, the one attached to the charge-bearing carbon.

A similar set of reactions must also occur in AlCl₃/pentane, which elicits the question: Where does the hydride come from that quenches the 1-chloro-2-norbornyl cation? There are only two possibilities: the substrate or a product derived from the substrate and the solvent. To answer this question, the reaction was run in pentane and pentane-*d*₁₂ and the product mixture analyzed by GC/MS. In pentane two significant observations were made: (1) Four dichloronorbornanes (**6–9**) (21 are theoretically possible) were formed in yields similar to that of 1-chloronorbornane (eq 3). This observation was never mentioned in the literature syntheses of 1-chloronorbornane. Although the four new products were not definitively identified, each of them clearly had a chlorine at C-1 and likely did not have a chlorine at C-4 or C-7. This suggestion is based on the very prominent peaks in the mass spectrum of each compound at *m/z* 101 and 103, which are due to the cyclopentadienyl cation **10** and *m/z* 129 and 131 due to the 1-chloronorbornyl cation. One can reasonably assign the compounds as 1,2-*exo*- (**6**), 1,2-*endo*- (**7**), 1,3-*exo*- (**9**), and 1,3-*endo*-dichloronorbornane (**10**).¹² (2) Numerous trace products with molecular weights around 130/132 (±2), the molecular weight of

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TABLE 1. ^1H and ^{13}C Chemical Shifts of **3** and **5**

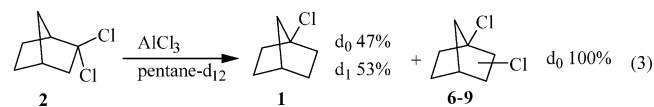
position	3		5 ^{2,10,11}	
	^1H	^{13}C	^1H	^{13}C
1	4.93	76.9	4.83	59.3
2	—	284.5	—	260.1
3	3.48, ~3.6 ^a	61.0	3.49	50.4
4	3.40	42.5	3.20	39.4
5	2.32, ~3.6 ^a	22.2	1.41	25.3
6	1.66, 2.07	40.5	2.00, 2.81	34.1
7	2.47	36.0 ^b	2.04	41.4

^a C-3 and C-5 have hydrogens that overlap at ~3.6. ^b C-7 is severely broadened, even at $-100\text{ }^\circ\text{C}$, suggesting that an unknown dynamic reaction is occurring

1-chloronorbornane, are also produced.



When the reaction was repeated in pentane- d_{12} , the resulting 1-chloronorbornane consisted of 47% d_0 and 53% d_1 (eq 3). Interestingly, none of the dichloronorbornanes was deuterated (eq 3).



One may conclude from the labeling experiment that the hydride arises from both sources, substrate/product and solvent. Alkanes, including pentane, isomerize in the

presence of AlCl_3 .¹³ The isomerization of pentane is initiated by hydride abstraction, most likely from a secondary carbon, to form AlCl_3H^- (or AlCl_3D^-) which, in this instance, quenches the 1-chloro-2-norbornyl cation.

Experimental Section

In a 25-mL, three-necked, round-bottomed flask containing 0.175 g (1.07 mmol) of 2,2-dichloronorbornane in 5.0 g (6.8 mL) of pentane- d_{12} was added, under nitrogen, 0.070 g (0.53 mmol) of AlCl_3 via a sidearm attachment over 3 h. After the reaction mixture was stirred for an additional 40 h at room temperature, the pentane was decanted from the reaction sludge which in turn was washed with additional pentane. The combined pentane extracts were washed with brine and water, dried, and removed in vacuo. The residue was analyzed by GC/MS. The 1-chloronorbornane peak was identified by comparison to that of the known compound. The deuterium content of 1-chloronorbornane was determined from the peak areas of the molecular ions.

The NMR samples were prepared by standard techniques^{11,14} and the ^1H and ^{13}C spectra recorded on a 400 MHz instrument.

Acknowledgment. This work was supported by the Environmental Protection Agency, Office of Pollution Prevention and Toxics, Exposure Evaluation Division.

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