# The Addition of Hydrogen Chloride and Hydrobromic Acid to 2,3-Dideuterionorbornene

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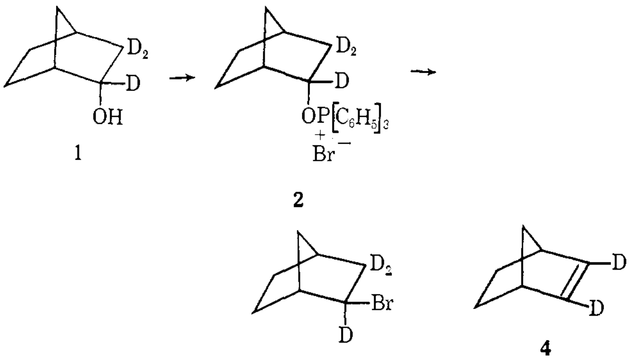
**Abstract:** The synthesis of 2,3-dideuterionorbornene and the ionic addition of hydrogen halides to it have been carried out. From the reaction of hydrogen chloride, about 50% of the product results from *exo–cis* addition without rearrangement. Of the portion of the product formed as a consequence of rearrangement, 38% arises from a 6,2-hydride shift and 12% from a Wagner–Merrwein rearrangement. In the reaction with hydrobromic acid, the percentages are 40, 46, and 14, respectively. Dehydrohalogenation of the *exo*- and *endo*-2-halonorbornanes occurs nearly exclusively by abstraction of the *exo*-vicinal proton by base. The mechanistic interpretation of these results is discussed.

The additions of hydrogen halides to the double bond of $\alpha,\beta$-unsaturated acids,[2] cyclopentenes,[3] and cyclohexenes[4,5] have been found, under polar conditions, to give the *trans* addition product. Recently, however, in the case of certain rigid cyclic olefins such as acenaphthalene,[6] indene,[7] and norbornene,[8] the polar additions of deuterium bromide and deuteriobromic acid have been found to occur to give a large percentage of the *cis* addition products. Yet it is interesting to note that base dehydrohalogenation of the halogenated adduct of acenaphthalene undergoes a *trans* elimination, while the norbornyl adduct undergoes a *cis* elimination. These elimination paths were employed, in fact, to substantiate the *cis* mode of addition of deuterium bromide to acenaphthalene and deuteriobromic acid to norbornene. The behavior of these systems presents a mechanistic dichotomy which suggests that there is possibly something unique to the norbornyl system that dictates ionic *cis* addition and *cis* elimination. Thus, an investigation of the addition of hydrogen chloride and hydrobromic acid under polar conditions to 2,3-dideuterionorbornene and the base elimination reactions of the product halides was carried out. The olefin, 2,3-dideuterionorbornene (**4**), alleviates some of the difficulties encountered in the addition of deuteriobromic acid to norbornene,[8] because the product formed from a 6,2-hydride shift and the Wagner–Meerwein rearrangement as well as from an *exo–cis* addition could be detected and quantitatively determined by nmr.

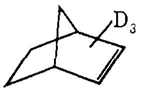
## Results and Discussion

The synthesis of 2,3-dideuterionorbornene (**4**) was accomplished by treating *endo*-2-norborneol-2,3,3-$d_3$ (**1**)[9] with triphenylphosphine and bromine,[10] pyrolyzing the intermediate, *endo*-2-norbornoxytriphenylphosphonium bromide-2,3,3-$d_3$ (**2**), to obtain *exo*-2-bromonorbornane-2,3,3-$d_3$ (**3**), and dehydrobrominating this product with *t*-hexoxide in *t*-hexyl alcohol to afford **4**.



1 2 3 4

The isotopic purities of compounds **1**, **3**, and **4** were determined by quantitative nmr analysis. On two different runs compounds **1**, **3**, and **4** averaged 96.2, 90.0, and 91.8% purity, respectively. Mass spectral analysis of **4** was 8.1% $d_3$, 89.3% $d_2$, 2.4% $d_1$, and 0.1% $d_0$. The 8.1% $d_3$ (**5**) can be best explained by the following considerations: reduction[11] of 3,3-dideuterionorcamphor with lithium aluminum deuteride yields about 9% *exo*-2-norborneol-2,3,3-$d_3$ (**6**). It has been found that treatment of optically active *exo*-2-norborneol with triphenylphosphine and bromine[12] provides *exo*-2-bromonorbornane which has undergone about 80% racemization.



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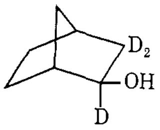

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The ionic addition of hydrogen chloride[13] to 2,3-dideuterionorbornene (**4**) was carried out at −78° for 1 hr. The ratio of *exo*- to *endo*-chloride was 98.5:1.5.[9] About 49.9% of the addition product **8** was a result

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[2] W. R. Vaughan, R. L. Craven, R. Q. Little, and A. C. Schoenthaler, *J. Am. Chem. Soc.*, **77**, 1994 (1955).

[3] G. S. Hammond and C. H. Collins, *ibid.*, **82**, 4323 (1960).

[4] G. S. Hammond and T. D. Newitt, *ibid.*, **76**, 121 (1954).

[5] R. C. Fahey and R. A. Smith, *ibid.*, **86**, 5035 (1964).

[6] M. J. S. Dewar and R. C. Fahey, *ibid.*, **85**, 2245 (1963).

[7] M. J. S. Dewar and R. C. Fahey, *ibid.*, **85**, 2248 (1963).

[8] H. Kwart and J. L. Nyce, *ibid.*, **86**, 2601 (1964).

[9] J. K. Stille and F. M. Sonnenberg, *ibid.*, **88**, 4915 (1966).

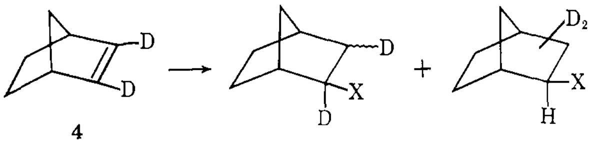
[10] We wish to thank J. P. Schaefer (University of Arizona, Tuscon, Ariz.) for sending us this procedure prior to publication; see J. P. Schaefer and D. S. Weinberg, *J. Org. Chem.*, **30**, 2635 (1965).

[11] C. F. Wilcox, M. Sexton, and M. F. Wilcox, *ibid.*, **28**, 1079 (1963).

[12] J. P. Schaefer and D. S. Weinberg, *ibid.*, **30**, 2639 (1965).

[13] H. Kwart and R. K. Miller, *J. Am. Chem. Soc.*, **78**, 5008 (1956).

of skeletal rearrangements, as determined by nmr analysis and detected by the appearance of a proton instead of a deuterium atom on the carbon bearing the chloride.



4

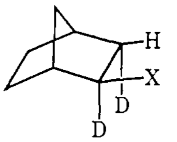
X
7 = Cl
9 = Br

X
8 = Cl
10 = Br

The other 50.1%, **7**, had the chloride in the *exo*-2-position with an *endo*-deuterium geminal.

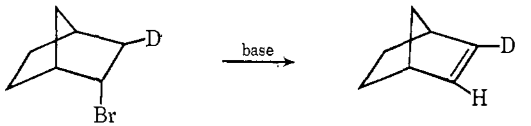
The polar addition of hydrobromic acid[8] to 2,3-dideuterionorbornene (**4**) was carried out at 60° for 3 hr to afford 59.4% of **10**, as a consequence of rearrangement, and 40.6% of **9** as determined by nmr. The ratio of *endo*- to *exo*-bromide by vpc analysis was 2.6:97.4.

The geometry of the deuterium in the three position of **7** or **9**, *exo* or *endo*, could not be ascertained with certainty from the nmr spectra. From a consideration of the reports of *exo* and *exo–cis* additions[14–18] to norbornene, a preliminary assumption was made in assigning the proton in the *exo*-three position (**11**, **12**). The geometry of the deuterium could be determined through a hydrogen halide or deuterium halide elimination with base, if the proton (deuteron) *exo* or *endo* which is removed in this reaction could be determined.



X
11 = Cl
12 = Br

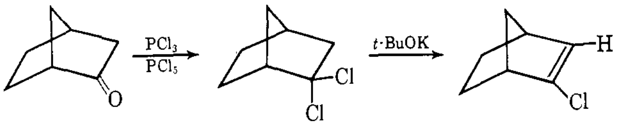
Bimolecular *cis* elimination reactions usually are only observed in cyclic systems because the rotation of the leaving group about the carbon atom is restricted. In the norbornyl system a perfect *trans* elimination is impossible due to the lack of coplanarity (*ca.* 120° dihedral angle) of the leaving groups. In the light of this evidence, it was recently postulated[8] that the product obtained from the reaction of *endo*-2-bromonorbornane-*exo*-3-$d_1$ with *t*-hexoxide in *t*-hexyl alcohol would be 2-deuterionorbornene (**13**). This prediction was based both on the preference for *cis* elimination in the norbornyl system and the added reenforcement of a primary deuterium isotopic effect which would be expected to outweigh the abstraction of the *exo* proton.



13

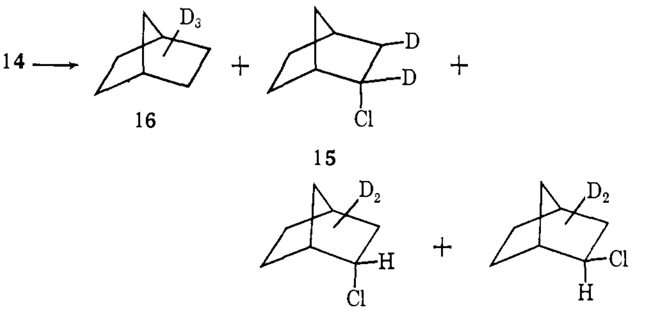
We felt, therefore, that it would be of interest to determine whether *cis* elimination would indeed occur over *trans* elimination by preparing *endo*-2-chloronorbornane-*exo*-2,3-$d_2$ (**15**) and performing the base elimination with *t*-hexoxide in *t*-hexyl alcohol.

The model compound, **15**, was prepared from norcamphor by known methods.[19,20] The addition of deuterium to the double bond of norbornene in the presence of a heterogeneous catalyst is known to add *exo–cis*.[21] Moreover, whether one or two substituents is attached to the double bond of norbornene, hydrogenation occurs *exo–cis*.[22,23]



14

The addition of deuterium to 2-chloronorbornene (**14**) to form **15**, in an ether solvent with or without added sodium acetate or other solvents, is accompanied by deuteriumolysis resulting in the formation of norbornane-$d_3$ (**16**), the major product, as well as rearranged chlorides **17** and **8**. The sample of norbornyl chloride employed for the elimination reaction contained 84% **15**, 6% **17**, and 10% **8**, as determined by integration of the nmr spectrum.



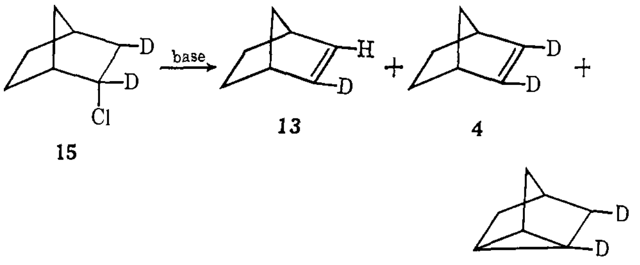
16

15

17

8

Dehydrochlorination of the mixture of **15**, **17**, and **8** with *t*-hexoxide in *t*-hexyl alcohol[24] yielded norbornene and nortricyclene products in a ratio of 89:11 as determined by vpc analysis. It was found that under the same conditions, *exo*-2-chloronorbornane affords



15

13

4

18

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(14) H. A. Bruson and T. W. Riener, *J. Am. Chem. Soc.*, **67**, 723 (1945).

(15) L. Schmerling, U. S. Patent 2,480,267; *Chem. Abstr.*, **44**, 1136 (1950).

(16) T. G. Traylor and A. W. Baker, *Tetrahedron Letters*, No. **19**, 14 (1959).

(17) C. W. Bird, R. C. Cookson, J. Hudec, and R. O. Williams, *J. Chem. Soc.*, 410 (1963).

(18) J. Meinwald, Y. C. Meinwald, and T. N. Baker, *J. Am. Chem. Soc.*, **85**, 2513 (1963).

(19) R. L. Bixler and C. Niemann, *J. Org. Chem.*, **23**, 742 (1958).

(20) N. A. LeBel, *J. Am. Chem. Soc.*, **82**, 623 (1960).

(21) D. A. Arnold, D. J. Trecker, and E. B. Whipple, *ibid.*, **87**, 2596 (1965).

(22) R. A. Finnegan and R. S. McNees, *J. Org. Chem.*, **29**, 3234 (1964).

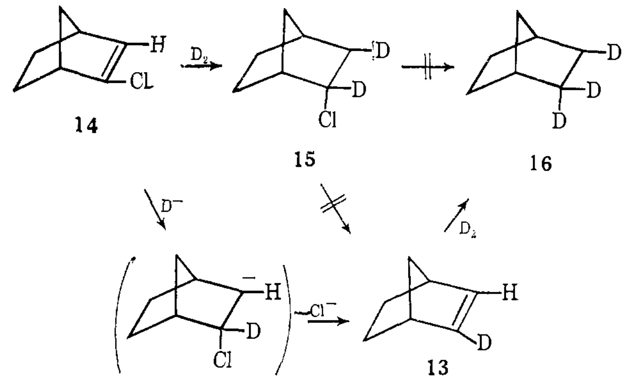
(23) K. Alder and W. Roth, *Ber.*, **87**, 161 (1954).

(24) H. Kwart, T. Takeshita, and J. L. Nyce, *J. Am. Chem. Soc.*, **86**, 2606 (1964).

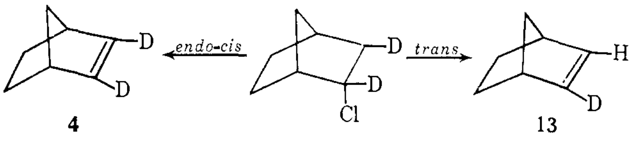
only norbornene; thus the nortricyclene (**18**) must only be forming from the *endo*-chloride.

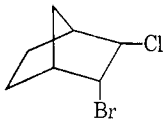
The percentages of **13** and **4** were found to be 86:14, respectively. Thus, *trans* elimination is favored over *endo–cis* by a factor of about 6.0.

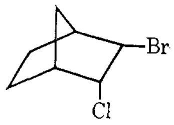
The formation of **16** during deuteration can be rationalized by the following sequence of reactions. That **16** is not formed from **15** either by an elimination of deuterium chloride to give **13** followed by deuteration or by deuteriumolysis of **15** was demonstrated by the fact that **15** was found to be unreactive under the reaction conditions.



Even though the primary deuterium isotope effect ($k_H/k_D \simeq 7.5$) favors the removal of the *endo*-2-proton by base from **15**, steric considerations tend to make this mode of attack less likely. Of primary importance in E2 elimination reactions is the ease of removal of the *exo*-3-deuterium atom, and thus *trans* elimination is forced. This result was not unexpected in light of recent work[25] on various 2,3-dihalonorbornanes. Even though it is well known that bromide is a better leaving group than chloride, it was found that dehydrohalogenation of **19a** and **b** gave 2-bromonorbornene and 2-chloronorbornene, respectively.

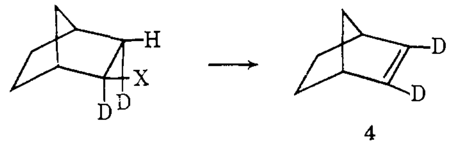



19a


19b

Examination[26,27] of the relative rates of elimination of 2,3-halonorbornenes showed that *exo–cis* elimination was faster than *trans*. From our results, it is evident that the dehydrohalogenation of halonorbornanes would fall in the order *exo–cis* > *trans* > *endo–cis*, and of utmost importance is the fact that it is the *exo* proton which is preferentially removed by base.

Thus, if 100% *exo–cis* elimination occurred with chloride containing 50.1% **11**, the product obtained should be 50.1% **4**. Dehydrochlorination of the mixture of **7** and **8** with *t*-hexoxide in *t*-hexyl alcohol affords only norbornene (no nortricyclene), 48.9% of which is **4** as determined by nmr. Therefore, *exo–cis* elimination occurs to the extent of 97.6%. Dehydrobromination of **9** and **10** affords olefin, 38.5% of which is **4**; thus, *exo–cis* elimination occurs to the extent of 94.8%. The addition of deuteriobromic acid to norbornene had been reported to proceed with 46% *exo–cis* addition.[8]



X
11=Cl
12=Br
4

Since it has been shown clearly that protonation occurs from the *exo* side, the first three products expected from the ionic addition of hydrogen halides to 2,3-dideuterionorbornene (4) are those from an *exo-cis* addition, **20**, a Wagner–Meerwein rearrangement, **21**, and a 6,2-hydride shift, **22** (Figure 1).

By nmr analysis it was possible to determine the amount of Wagner–Meerwein rearrangement, **21**, and 6,2-hydride shift, **22**. From the addition of hydrogen chloride to **4**, 12.0% of the product **21** was formed *via* a Wagner–Meerwein rearrangement, while 37.9% of the product **22** was formed *via* a 6,2-hydride shift. Addition of hydrobromic acid resulted in 13.8% of **21** and 45.6% of **22**. Thus, a 6,2-hydride shift accounts for about three-fourths of the deuterium scramblings while a Wagner–Meerwein rearrangement accounts for one-fourth. This finding is quite comparable to the results[9] obtained from the reaction of *endo*-2-norborneol-2,3,3-$d_3$ with thionyl chloride in ether, pyridine, dioxane, or ether with added pyridine.

Since the nonclassical carbonium ion should give equal amounts of **20** and **21**, the amount of **20** obtained from some other mechanism such as a concerted *cis* addition would be 38.1% and 26.8% from hydrogen chloride and hydrobromic acid addition to **4**, respectively.

It appears quite striking that the hydrogen chloride addition gives about 10% more *exo–cis* addition than does hydrobromic acid; however, this is probably due to different reaction conditions.

## Experimental Section[28]

***endo*-2-Norbornoxytriphenylphosphonium Bromide-2,3,3-$d_3$ (2).**[10] From 19.0 g (0.165 mole) of *endo*-2-norborneol-2,3,3-$d_3$,[9] 43.4 g (0.165 mole) of triphenylphosphine in 140 ml of triglyme, and 26.6 g (0.165 mole) of bromine in 40 ml of triglyme was obtained, after work-up in a drybox, 81.4 g (108%) of a white solid containing some absorbed triglyme.

**Decomposition of *endo*-2-Norbornoxytriphenylphosphonium Bromide-2,3,3,-$d_3$ (2).**[10] Pyrolysis of dry **2** at 40–120° (0.1 mm) afforded, after redistillation, 17.7 g (60.3%) of *exo*-2-bromonorbornane-2,3,3-$d_3$ (**3**), bp 78–80° (30 mm), $n^{19}$D 1.5115 (lit.[10] bp 80° (28 mm), $n^{24}$D 1.5149). Nmr analysis showed the incorporation of

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[25] N. A. LeBel, P. D. Beirne, and P. M. Subramanian, *J. Am. Chem. Soc.*, **86**, 4144 (1964).

[26] S. J. Cristol and E. R. Hoegger, *ibid.*, **79**, 3438 (1957).

[27] N. A. LeBel, P. D. Beirne, E. R. Karger, J. C. Powers, and P. M. Subramanian, *ibid.*, **85**, 3199 (1963).

[28] Gas chromatographic analyses were carried out with the F & M Model 500 instrument using either a 10% diisodecyl phthalate (8 ft × 0.25 in.) or a 5% Zonyl E-7 (40 ft × 0.25 in.) column. A Varian A-60 was used for nmr spectra with tetramethylsilane as the internal standard and carbon tetrachloride as the solvent. Infrared analyses were run on a Perkin-Elmer Infracord.

2.664 and 2.721 deuterium atoms per molecule (88.8 and 90.7% purity) on different runs. Vpc analysis using a 5% Zonyl E-7 (40 ft × 0.25 in.) column at 75° and a helium flow of 100 cc/min showed that only *exo*-2-bromonorbornane was present.

**Dehydrobromination of *exo*-2-Bromonorbornane-2,3,3-$d_3$ (3).** The dehydrobromination was carried out with *t*-hexoxide as described[8] with slight modification. After formation of *t*-hexoxide from 51.0 g (0.5 mole) of *t*-hexyl alcohol and 3.0 g (0.075 g-atom) of potassium, 8.9 g (0.05 mole) of *exo*-2-bromonorbornane-2,3,3-$d_3$ (3) was added. The solution was heated under reflux for 24 hr while sweeping continuously with nitrogen and collecting the product in a trap cooled in a Dry Ice-isopropyl alcohol bath. The contents of the trap were distilled after adding small amounts of potassium, and the cut from 80 to 105° was collected and redistilled several times until 2,3-dideuterionorbornene solidified in the receiver. There was recovered 2.18 g (45.6%) of solid after sublimation, bp 84-96°. Nmr analysis showed the presence of 1.848 atoms of deuterium per molecule for **4** (92.4% purity). Mass spectral analysis of **4** showed the following: 8.1% $d_3$, 89.3% $d_2$, 2.4% $d_1$, and 0.1% $d_0$. On another run, nmr indicated 2.736 atoms of deuterium per molecule for **4** (91.2% purity). Vpc analysis using a 10% diisodecyl phthalate (8 ft × 0.25 in.) column at 45° and a helium flow of 67 cc/min showed that only norbornene was present.

**Polar Addition of Hydrogen Chloride to 2,3-Dideuterionorbornene (4).** The addition of dry hydrogen chloride was carried out over a period of 1 hr in pentane at −78° as described.[13] From 1.44 g (0.015 mole) of **4** in 15 ml of pentane was obtained 1.68 g (84.3%) of dideuterio-*exo*-2-chloronorbornane. Integration of the nmr spectrum was carried out to obtain the amount of *exo–cis*, Wagner-Meerwein, and 6.2-hydride product from the relative ratios of hydrogens on position 2,1 plus 4, and the remaining positions.[29] Retention times of 47 min for the *endo* epimer and 50 min for the *exo* epimer were observed using a 5% Zonyl E-7 (40 ft × 0.25 in.) column at 95° and a helium flow of 86 cc/min; the ratio of *endo*- to *exo*-chloride was 1.5:98.5.

**Dehydrochlorination of Dideuterio-*exo*-2-chloronorbornane.** The same procedure as described for the elimination reaction of *exo*-2-bromonorbornane-2,3,3-$d_3$ (3) was followed. From 10.2 g (0.1 mole) of *t*-hexyl alcohol, 0.6 g (0.015 g-atom) of potassium, and 1.32 g (0.1 mole) of dideuterio-*exo*-2-chloronorbornane was obtained 0.382 g (39.8%) of dideuterionorborene after sublimation. Integration of the appropriate signals of the nmr spectrum showed that 48.9% of the product was 2,3-dideuterionorbornene (4).[29] Vpc analysis at 45° showed the presence of no nortricyclene.

**Polar Addition of Hydrobromic Acid to 2,3-Dideuterionorbornene (4).** The addition of 48% hydrobromic acid was carried out at 60° for 3 hr as described.[8] To 0.96 g (0.1 mole) of 2,3-dideuterionorborene (4) and 3.3 g (0.041 mole) of hydrobromic acid was obtained 1.26 g (71.3%) of dideuterio-*exo*-2-bromonorbornane. Nmr integration was carried out as described under the polar addition of hydrogen chloride to 2,3-dideuterionorbornane (4).[29] Retention times of 123 min for the *endo* epimer and 138 min for the *exo* epimer was observed using a 5% Zonyl E-7 (40 ft × 0.25 in.) column at 80° and a helium flow of 100 cc/min. The ratio was 2.6:97.4, respectively.

**Dehydrobromination of Dideuterio-*exo*-2-Bromonorbornane.** The same procedure as described for the elimination reaction of *exo*-2-bromonorbornane-2,3,3-$d_3$ (3) was followed. From 10.2 g (0.1 mole) of *t*-hexyl alcohol, 0.6 g (0.015 g-atom) of potassium, and 1.018 g (0.0063 mole) of dideuterio-*exo*-2-bromonorbornane was obtained 0.203 g (33.6%) of dideuterionorbornane after sublimation. Integration of the appropriate signals of the nmr spectrum showed that 38.5% of the product was 2,3-dideuterionorborene (4).[29] Vpc analysis at 45° showed only norborene. No nortricyclene was present.

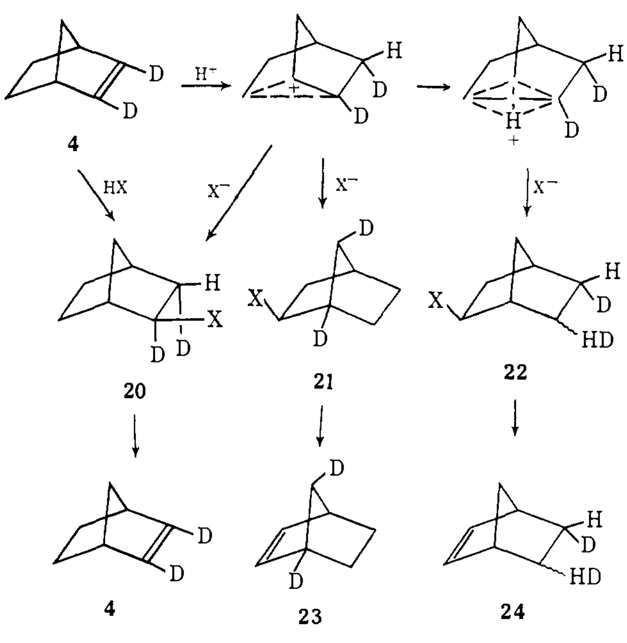

Figure 1.

***endo*-2-Chloronorbornane-*exo*-2,3-$d_2$ (15).** To a solution of 10.3 g (0.08 mole) of 2-chloronorbornene (**14**)[19,20] in 60 ml of ether was added 0.4 g of platinum oxide. Deuterium was allowed to enter, and the uptake was 165% after 1 day. Filtration, removal of the ether, and distillation at bp 106-110° (lit.[30] bp 105.7°) afforded 3.06 g (38.7%) of norbornane-$d_3$ after sublimation. Vacuum distillation of the residue yielded 1.92 g (18.1%) of a low-melting solid, bp 54-56° (16 mm) (lit.[31] bp 51-53° (17 mm)). Integration of the appropriate signals of the nmr spectrum showed that 84% was **15**, 6% was **17**, and 10% was **8**.[29] Vpc analyses on different runs indicated that the ratio of *endo*- to *exo*-2-chloronorbornane was 7.9-4.2:92.1-95.8 in ether, using a 5% Zonyl E-7 (40 ft × 0.25 in.) column at 75° and a helium flow of 100 ml/min. The retention times were 9 and 97 min, respectively. Similar results were obtained with added sodium acetate to the hydrogenation mixture.

**Dehydrochlorination of *endo*-2-Chloronorbornane-*exo*-2,3-$d_2$.** The same procedure as described for the elimination reaction of *exo*-2-bromonorbornane-2,3,3-$d_3$ (3) was followed. From 10.2 g (0.1 mole) of *t*-hexyl alcohol, 0.6 g (0.015 g-atom) of potassium, and 1.46 g (0.011 mole) of **15** was obtained 0.231 g (21.7%) after sublimation. Vpc analysis using a 10% diisodecyl phthalate (8 ft × 0.25 in.) column at 45° and a helium flow of 67 cc/min showed the ratio of norbornene to nortricyclene to be 89:11. The retention times were 15 and 19 min, respectively. Integration of the appropriate signals of the nmr spectrum showed the percentage of **8** to **13** to be 86:14.[29]

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(29) The high ratio of 6,2-hydride shift (6,2-H) *vs.* Wagner-Meerwein (W-M) product represents a minimum value, since all the possible products from combinations of successive W-M rearrangements and 6,2-H are the same whether or not a W-M or a 6,2-H takes place first. Therefore the percentages represent the ratio of 6,2-H plus products from other combinations to W-M plus products from other combinations. Complete equilibration, however, involving only two successive 6,2-H and W-M steps is not observed in the solvolysis of norbornyl acetate; see J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, 76, 4801 (1954).

(30) P. von R. Schleyer, *ibid.*, **80**, 1700 (1958).

(31) J. D. Roberts, W. Bennett, and R. Armstrong, *ibid.*, **72**, 3329 (1950).