Additions of Protonic Acids to 2,3-Dideuterionorbornene.[1] Evidence for the Existence of a Classical Norbornyl Cation

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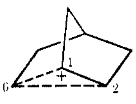
The synthesis of 2,3-dideuterionorbornene (**1**) and the additions of the protonic acids, hydrogen chloride, hydrogen bromide, hydrogen fluoride, formic acid, phenol, and methanol, to it gave only *exo*-norbornyl adducts. The additions of hydrogen chloride and hydrogen bromide gave greater than 50% of product resulting from an exo-cis addition. In the additions of formic acid, methanol, and hydrogen fluoride, the amounts of products resulting from exo-cis addition and Wagner-Meerwein rearrangement were essentially equal. A mechanistic interpretation of the data is presented, in which a classical norbornyl cation is formed in the course of addition of hydrogen chloride and hydrogen bromide to norbornene.

The electrophilic additions of protonic acids to norbornene usually proceed to give exo-substituted products,[4-8] *via* a positively charged intermediate, the norbornyl cation. Three different structures of the norbornyl cation in solution, a nonclassical bridged ion (**2**),[9] a localized classical ion (**3**),[10] and an edge-protonated nortricyclonium ion (**4**),[11,12] have been suggested.



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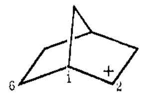

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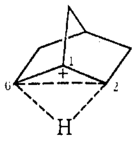

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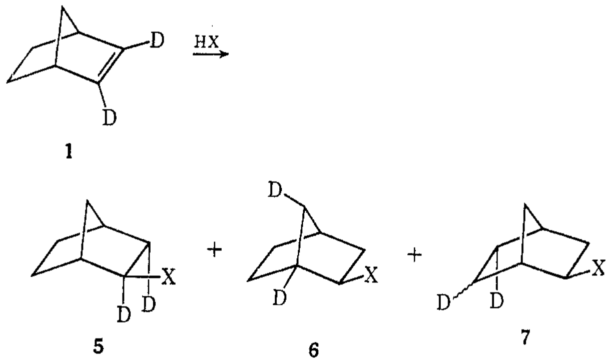
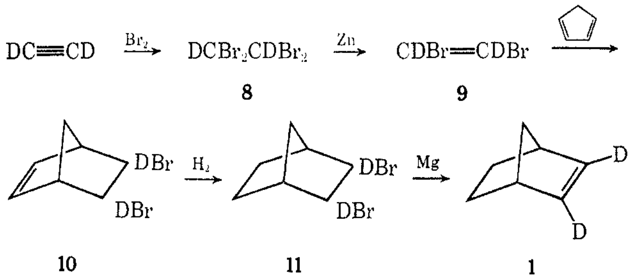
The deuterium labeled olefin, 2,3-dideuterionorbornene (**1**), was synthesized to facilitate the determination of the stereochemical courses of additions to this bicyclic system. Determination of the deuterium distribution in the product mixtures by analysis of the nmr spectra would be more accurate in the additions of protonic acids to **1** than in the additions of deuterionic acids to norbornene. The intermediate deuterium labeled norbornyl cation from the protonation of **1** suffers nucleophilic capture to give deuterium-labeled products. Capture at C-2 should yield **5**, the exo-cis addition product.[13] Capture at C-1 would yield **6**, resulting from a Wagner-Meerwein rearrangement of **3** or capture of **2** or **4** at C-1, and capture of the much less favored 6,2-hydride shift intermediate[12] would afford **7**.



Results

Synthesis of 1.—Dideuterioacetylene, generated from calcium carbide and deuterium oxide, was passed directly into molecular bromine to yield *sym*-tetrabromodideuterioethane (**8**). The debromination of **8** with zinc afforded a mixture of *cis*- and *trans*-1,2-dibromo-1,2-dideuterioethylene (**9**).[14] The Diels-Alder reaction of **9** and cyclopentadiene gave a mixture of *cis*- and *trans*-5,6-dibromo-5,6-dideuterionorbornene (**10**), which, when hydrogenated, yielded the corresponding 2,3-dibromo-2,3-dideuterionorbornanes (**11**).[14] Debromination of **11** with magnesium afforded **1**.[15] Mass spectral analysis of **1** showed it to be 95% d_2, 2% d_1, and 3% d_0 material. The signal at δ 5.93 ppm (vinyl hydrogen) was nearly absent in the nmr spectrum of **1**.



Additions of HX to 1.—The additions of compounds of general formula HX (X = Cl, Br, F, OCHO, OCH_3, OC_6H_5) to **1** gave products **5-7**, the relative amounts of which were determined by analysis of the nmr spectrum of each product mixture. Corrections for the small amount of vinyl hydrogen present in **1** were incorporated to give the results summarized in Table I.

Deuterium chloride has been reported to add rapidly to norbornene at −78° in methylene chloride to yield 60% of product resulting from an exo-cis addition, 35% from a Wagner-Meerwein rearrangement, and 5%

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[3] Abstracted in part from the Ph.D. thesis of R. D. Hughes, University of Iowa, May 1970. National Defense Education Act Fellow, 1966-1969, Phillips Petroleum Fellow, 1969-1970.

[4] T. G. Traylor and A. W. Baker, *Tetrahedron Lett.*, No. 19, 14 (1959).

[5] L. Schmerling, J. P. Luvisi, and R. W. Welch, *J. Amer. Chem. Soc.*, **78**, 2819 (1956).

[6] H. A. Bruson and T. W. Riener, *ibid.*, **67**, 723 (1945).

[7] L. Schmerling, *ibid.*, **68**, 195 (1946).

[8] J. D. Roberts, E. R. Trumbull, Jr., W. Bennett, and R. Armstrong, *ibid.*, **72**, 3116 (1950).

[9] S. Winstein, *ibid.*, **87**, 376 (1965).

[10] H. C. Brown and M. H. Rei, *ibid.*, **90**, 6216 (1968).

[11] G. A. Olah, A. Commeyras, and C. Y. Lui, *ibid.*, **90**, 3882 (1968).

[12] G. A. Olah and A. M. White, *ibid.*, **91**, 3957 (1969).

[13] Exo attack on the trigonal C-2 in this system is generally accepted to be preferred over endo attack; see J. A. Berson, "Molecular Rearrangements," Part I, P. de Mayo, Ed., Interscience, New York, N. Y., 1963, pp 130-133.

[14] N. A. Le Bel, P. D. Beirne, E. R. Karger, J. C. Powers, and P. M. Subramanian, *J. Amer. Chem. Soc.*, **85**, 3199 (1963).

[15] L. Schmerling, J. P. Luvisi, and R. W. Welch, *ibid.*, **78**, 2819 (1956).

TABLE I

PROTONIC ACID ADDITIONS TO 1

Acid (HX) and catalyst	Solvent	Temp, °C	Time, min	Product composition, %[a] 5	6	7
HCl	CH_2Cl_2	−78	5	56	42	$\sim$2
HCl	n-C_5H_{12}	−78	60	59	39	$\sim$2
HCl	$(C_2H_5)_2O$	27	190	65	27	8
HBr	CH_2Cl_2	−45	5.5	54	40	$\sim$5
HBr	H_2O	60	180	52	36	11
HOC_6H_5, BF_3	CH_2Cl_2	−22	240	47	39	14
HF	CH_2Cl_2	−78	5	22	24	54
HOCHO, BF_3	CH_2Cl_2	−22	60	47	46	7
$HOCH_3$, H^+	CH_3OH	Reflux	1290	38	42	20

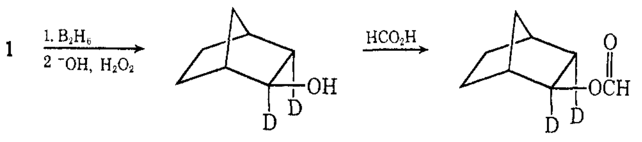
[a] Obtained from nmr spectra recorded with a Varian A-60 spectrometer as 20–30% solutions in $CDCl_3$ or C_6H_6 with tetramethylsilane as the internal standard. Product ratios were determined from the mean average of five tracings of the integral and were corrected for deuterium content as determined by mass spectra. These values are correct within ±2%, with the exception of the values 2 and 5% for **7** which were obtained by difference through normalization to 100% deuterium content.

from a 6,2-hydride shift.[16] Under similar conditions in chloroform, the reaction proceeds to completion in 2 min with 55% of the product resulting from exo–cis addition and 45% from a Wagner–Meerwein rearrangement.[17] The addition of hydrogen chloride to **1** was complete in 5 min at −78° in methylene chloride with **5**, **6**, and **7** (X = Cl) formed in the ratio of 56:42:2, respectively. Contrary to an earlier report, we were not able to detect a significant amount of 6,2-hydride shift product.[18] When the product mixture was placed back under the reaction conditions for an additional 50 min, the product ratio of **5**:**6**:**7** had only changed to 50:47:3. Apparently prolonged reaction times facilitated a small amount of solvolysis of the product chlorides and subsequently led to additional rearrangement. Less polar solvents such as pentane and ether were found to suppress rearrangement, and hence more **5** was found with these solvents. In all the additions of hydrogen chloride to **1**, only *exo*-norbornyl chloride was formed, to the exclusion of the endo isomer, as determined by vpc analysis.

The polar addition of anhydrous hydrogen bromide to **1** in methylene chloride at −45° was complete in 5.5 min with **5**, **6**, **7** (X = Br) produced in a ratio of 54:40:5, respectively. Deuteriobromic acid (48%) has been reported to add to norbornene to give 46% exo–cis addition and 51% rearrangement.[19] We carried out the addition of 48% hydrobromic acid to **1** and found the ratio of **5**:**6**:**7** (X = Br) to be 52:36:11, respectively. The products of these reactions undergo little or no change when subjected to the reaction conditions for prolonged times. No *endo*-norbornyl bromide was formed in any of the reactions, indicative of the absence of a radical reaction.[19]

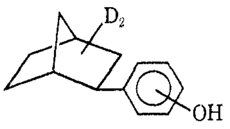
The addition of hydrogen fluoride to norbornene was reported to yield *exo*-norbornyl fluoride in low yields.[20] The reaction of hydrogen fluoride and **1** at −78° for 5 min in methylene chloride gave low yields of *exo*-norbornyl fluoride; the major product from the reaction was norbornene telomers. Analysis of the norbornyl fluoride product mixture showed a deuterium distribution of 22% at C-2 and 24% at C-1. This corresponds to a product mixture of **5**, **6**, and **7** (X = F) in a ratio of 22:24:54, respectively.

The boron trifluoride etherate catalyzed addition of formic acid to **1** proceeds to completion within 1 hr at −22° in methylene chloride. From careful integration of the appropriate signals in the nmr, it was determined that equimolar amounts (46%) of **5** and **6** (X = OCHO) and only 7% of **7** were formed. The uncatalyzed reaction required 48 hr at room temperature to proceed to completion with yields of **5**, **6**, **7** of 47, 42, and 11%, respectively. When an independently synthesized sample of *endo,endo*-2,3-dideuterio-*exo*-2-norbornyl formate (**13**) was placed in methylene chloride at −22° with formic acid and boron trifluoride, no rearrangement to **6** (X = OCHO) occurred. Thus, the product formates from the addition reaction must be stable to solvolysis under the reaction conditions.



12 **13**

The condensation of phenol with camphene at 0° is reported to give only isobornyl phenyl ether, when catalyzed with boron trifluoride etherate.[21] Under similar conditions **1** formed predominately C-alkylated phenols **14**, presumably the ortho and para isomers. The addition of phenol to **1** at −22° in methylene chloride with a boron trifluoride etherate catalyst was nearly complete after 4 hr to yield the O-alkylated phenol **15** as the major product. The distribution of deuterium in the final product corresponded to a ratio of 47:39:14 for **5**, **6**, and **7** (X = OC_6H_5), respectively.



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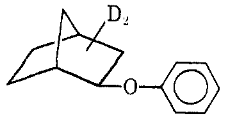

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endo-Trimethylenenorbornene has been reported to undergo a sulfuric acid catalyzed reaction with methanol to give 15% of unrearranged addition product and 85% of product due to a Wagner–Meerwein rearrangement.[22] With deuteriomethanol the unrearranged addition product was determined to be the result of an exo–cis addition. The sulfuric acid catalyzed addition of methanol to **1** in excess refluxing methanol yielded a product mixture in which 0.38 atoms of the deuterium were located at C-2, 0.42 atoms at C-1, and the remainder at the other positions. If one makes the reasonable assumption that no deuteride shifts have occurred,[23] this distribution of deuterium corresponds to a ratio of 38:42:20 for **5**, **6**, and **7** (X = OCH_3), respectively. Similar results were obtained when the reaction was

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(16) H. C. Brown and K. T. Liu, *J. Amer. Chem. Soc.*, **89**, 3900 (1967).

(17) J. M. Brown and M. C. McIvor, *Chem. Commun.*, 238 (1969).

(18) J. K. Stille, F. M. Sonnenberg, and T. H. Kinstle, *J. Amer. Chem. Soc.*, **88**, 4922 (1966). The reported ratios of products resulting from exo–cis addition, Wagner–Meerwein rearrangement, and 6,2-hydride shift (50:12:38) were in error due to nmr instrumental errors in integration.

(19) H. Kwart and J. L. Nyce, *ibid.*, **86**, 2601 (1964).

(20) M. Hanack and W. Kaiser, *Justus Liebigs Ann. Chem.*, **657**, 12 (1962).

(21) W. F. Erman, *J. Amer. Chem. Soc.*, **86**, 2887 (1964).

(22) S. J. Cristol, L. K. Gaston, and D. W. Johnson, *Tetrahedron Lett.*, 185 (1963).

(23) A deuteride shift could occur only if the cation was long-lived enough for the unfavored 3,2-*endo*-hydride shift to take place. See ref 12.

carried out in methylene chloride with a fivefold excess of methanol. In all cases only exo products were formed.

Discussion

The preference of cis over trans addition of HX to norbornene has been estimated to be at least 10^2:1, but not more than 10^4:1, based on the limits of detectability of endo products.[24] No endo products were detected in any of the additions studied in this work. With hydrogen chloride and hydrogen bromide, exo–cis addition accounted for the majority of the total product.

The amount of rearrangement which occurs in additions to norbornene has been attributed to the ability of the electrophilic portion of the addend to stabilize the intermediate cation.[24] In the additions reported in this work the same stabilizing influence on the intermediate cation should be felt, regardless of the protonic reagent. Thus, the proportion of rearrangement in these additions must be governed by the difference in the nucleophilic character of X and the reaction conditions. In fact, the amount of rearrangement showed a dependence on the nature of the nucleophile in the order HF_2, CH_3OH, OCHO $\sim$ C_6H_5OH > Br > Cl. A significant dependence of the degree of rearrangement on the solvent (X = Cl, Br) or the reaction temperature for those cases tested (X = Br, OCHO) was not observed.

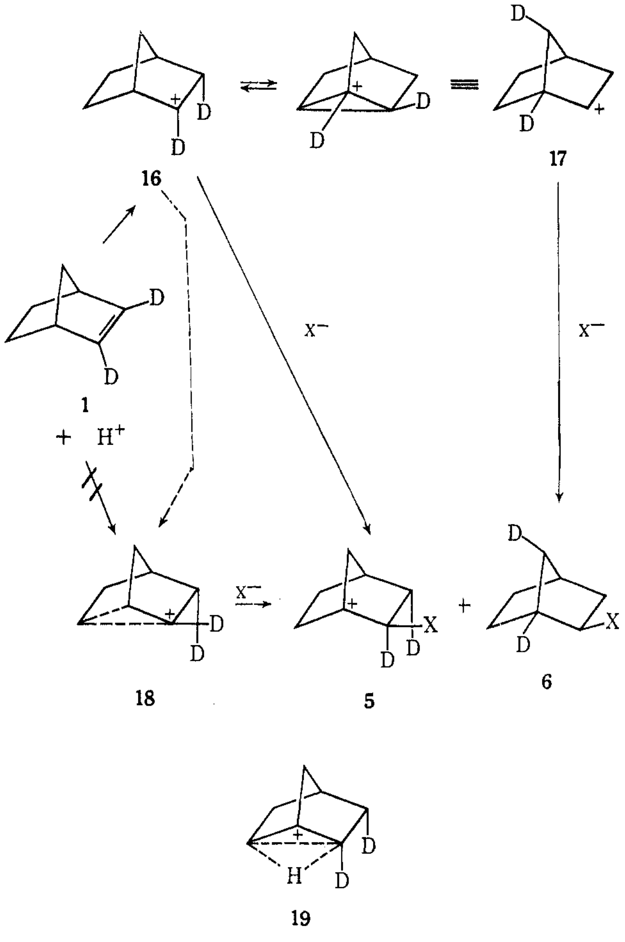
There are three possible intermediates which deserve consideration in the electrophilic additions to **1**: the classical norbornyl cation pair (**16** and **17**), the nonclassical norbornyl cation (**18**), and the nortricyclonium ion (**19**) (see Scheme I). Recent calculations suggest that under thermodynamically controlled conditions, **19** is more stable than either **16** or **17**.[25]

To invoke **19** as an intermediate in the additions to **1**, it must be concluded that the hydride shift which equilibrates positions C-1, C-2, and C-6 is extremely slow in comparison to the rate of capture by the nucleophile. This proton transfer would lead to the equivalence of C-1, C-2, and C-6 and hence, there should be equal probability of capture by X at these three sites. The amount of product formed *via* **19** in these additions could never, therefore, exceed that found for capture at C-6. Only when the protonic acid used was hydrogen fluoride was a significant amount of this product observed. In all other additions, and especially with hydrogen chloride and bromide, **19** cannot be an important intermediate in determining the product ratio.

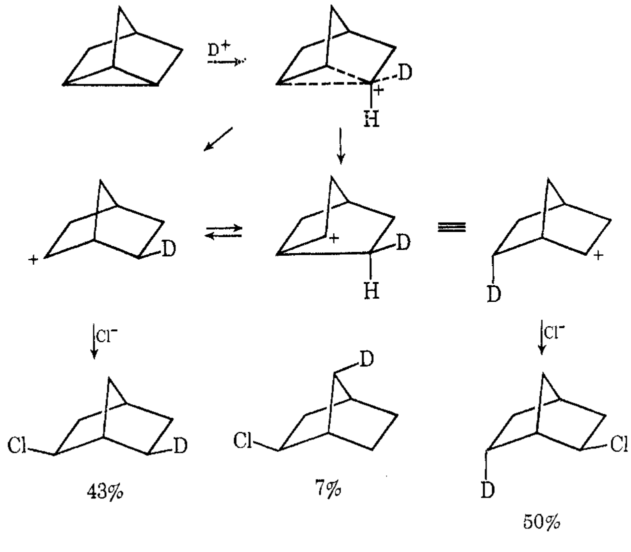
The addition of deuterium chloride to nortricyclene most certainly forms a protonated nortricyclonium ion as the initial intermediate[26,27] (Scheme II). This ion must rapidly and irreversibly leak to a classical or nonclassical norbornyl cation as no deuterium was found at positions C-1 or C-2 in the product mixture.[17] In the additions reported in this work, the product from capture of the cationic center at C-6 may best be accounted for by means of a competitive transannular hydride shift on the classical or nonclassical ions.

It is necessary to explain the 10–15% excess capture at C-2 over C-1 in the addition of hydrogen chloride and hydrogen bromide and the 8% excess in the addition of phenol. In all other additions, the amount of capture at these two sites is essentially equal. Neglecting the relatively small amounts of 6,2-hydride shift product observed (capture at C-6), several explanations may be offered. (1) Ion **16** is the initially formed intermediate and either (a) 85–90% leaks irreversibly to **18** while the remainder undergoes capture by X before rearrangement, or (b) the excess attack at C-2 represents capture of **16** before it reaches equilibrium with **17**, *i.e.*, capture of the rapidly equilibrating classical ions in an unsymmetrical state (see Scheme I). (2) The reaction pro-

SCHEME I



SCHEME II



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[24] T. G. Traylor, *Accounts Chem. Res.*, **2**, 152 (1969).

[25] G. Klopman, *J. Amer. Chem. Soc.*, **91**, 89 (1969).

[26] C. C. Lee and L. Gruber, *ibid.*, **90**, 3775 (1968).

[27] H. Fischer, H. Kollmar, H. O. Smith, and K. Miller, *Tetrahedron Lett.*, 5821 (1968).

ceeds by approximately 10–15% molecular (concerted or nearly concerted) addition of HX to **1** and about 85–90% through either (a) ion **18** in which capture occurs equally at C-1 and C-2 by X, or through (b) ion **16** which realizes complete equilibrium with **17** before capture by X.

Epoxidation, hydrogenation, and hydroboration, known concerted or molecular additions, add exo–cis to norbornene but add predominately endo–cis to 7,7-dimethylnorbornene.[28] The presence of 7,7-dimethyl substituents on norbornene, while successfully blocking the exo side to known molecular additions, has little or no effect upon blocking the additions of deuterium chloride and other ionic reagents from the exo side. It has been argued that electrophilic additions of protonic acids to **1** probably do not involve molecular addition. In light of this, explanations 2a and 2b are not likely.

On the basis of the results reported herein, it is not possible to distinguish between explanation 1a or 1b. Either pathway would successfully account for the relative proportions of attack at C-1 and C-2 by X. It would appear that only when X is chloride, bromide, or phenoxide is the rate of capture competitive with the rearrangement of **16** to **17** or leakage of **16** to **18**. It is important to point out that the results reported in Table I are not consistent with **18** as the sole product forming intermediate. Protonation must occur initially to give **16**, for if direct protonation to form **18** occurred, then an equal amount of product due to capture at C-1 and C-2 should always be observed.

Experimental Section[29]

2,3-Dideuterio-2,3-dibromonorbornene (11).—Hydrogenation of 83.2 g (0.328 mol) of **10**[14] in ethyl acetate over platinum oxide under 50 psi of hydrogen yielded, after distillation, 76.8 g (91%) of clear liquid, bp 55–90° (0.5–0.05 mm) [lit.[30] undeuterated, bp 59.5–70° (0.8 mm)].

Debromination of 11.[15] **Preparation of 1.**—To 270 ml of anhydrous diethyl ether, 7.25 g (0.299 g-atom) of magnesium turnings, and a small crystal of iodine was added with stirring 50.0 g (0.197 mol) of **11** in 55 ml of anhydrous diethyl ether at such a rate so as to maintain a gentle reflux. Once all the solution had been added, the pot and contents were heated at the reflux temperature for an additional 2 hr. The reaction mixture was poured onto ice and extracted with ether. The ethereal extracts from this run, a second run using the same quantities, and a third run using one-half the quantities cited above were combined and dried. The ether was removed by distillation, and the residual liquid was distilled through a 30-cm zigzag column to afford 30.09 g (64%) of **1**, bp 93.5–94° (lit.[31] undeuterated bp 96°), which solidified in the receiver.

Vpc analysis with a 15% SE-30 on Chromosorb W (20 ft by $^3/_8$ in.) column operated at 70° showed only norbornene was present. The signal at δ 5.92 (vinyl hydrogen) was absent in the nmr spectrum (CCl_4) of **1**. Mass spectral analysis showed the sample to be composed of 95% d_2, 2% d_1, and 3% d_0 isomers.

Addition of Hydrogen Chloride to 1. Methylene Chloride Solvent.—To 4 ml of methylene chloride in the reaction flask of an automatic hydrochlorinator,[32] cooled to −78°, was added 0.486 g (0.005 mol) of **1** in 8 ml of methylene chloride. The reaction mixture was stirred vigorously under the atmosphere of anhydrous hydrogen chloride for 5 min. The stirring was then stopped and the reaction mixture poured immediately onto enough 7–10% sodium bicarbonate solution to neutralize all of the acid present and render the mixture weakly basic. The product was extracted with additional methylene chloride solution and the extracts were dried. Evaporation of the methylene chloride afforded 0.443 g (68%) of *exo*-norbornyl chloride.

Vpc analysis on a 5% Zonyl E-7 (40 ft by $^1/_4$ in.) column at 95° and a helium flow of 85 ml/min showed only *exo*-norbornyl chloride was present. This column was shown to separate *exo*- and *endo*-norbornyl chloride in an earlier experiment under similar conditions. From the nmr spectrum (C_6H_6) the amounts of exo–cis addition, Wagner–Meerwein rearrangement, and 6,2-hydride shift were determined. The relative integrals at δ 3.64 (C-2 H), 2.25 (C-1 H), 2.06 (C-4 H), and 0.99–1.87 ppm (remainder of H) were measured. Mass spectral analysis showed the material to be greater than 95% d_2 isomer.

Pentane Solvent.[33]—Dry hydrogen chloride gas was passed over a period of 1 hr through a solution of 0.908 g (0.0095 mol) of **1** in 10 ml of dry pentane cooled to −78°. The mixture was then allowed to warm to room temperature and stand overnight. Distillation afforded 0.858 g (69%) of *exo*-norbornyl chloride, bp 54–56° (18 mm) [lit.[34] undeuterated bp 75° (41 mm)]. The product was shown to be homogeneous by vpc analysis on the Zonyl E-7 column. Mass spectral analysis showed the material to be greater than 95% d_2 isomer. From the nmr spectrum (C_6H_6) the product ratios were determined (Table I).

Diethyl Ether Solvent.—The addition of hydrogen chloride to **1** was carried out by passing dry hydrogen chloride over a solution of 0.508 g (0.0052 mol) of **1** in 25 ml of dry diethyl ether for a period of 3 hr at room temperature. Removal of the solvent and excess reactants under reduced pressure and distillation of the residue afforded a small amount of clear liquid, bp 74–78° (40 mm) [lit.[34] undeuterated bp 75° (41 mm)]. The nmr spectrum (C_6H_6) of the material was recorded and the product distribution was determined (Table I). Mass spectral analysis showed the material to be greater than 95% d_2 isomer.

Addition of Hydrogen Bromide to 1.—To a flask attached to a reservoir containing anhydrous hydrogen bromide was added 5 ml of methylene chloride. The mixture was cooled at −45° (chlorobenzene slush bath) with stirring. To the cooled solution was added 0.552 g (0.0575 mol) of **1** in 3 ml of methylene chloride. The reaction was allowed to proceed for 5 min; then the stirring was stopped and the contents of the reaction flask were poured onto 75 ml of 10% sodium bicarbonate solution. The product was extracted with additional methylene chloride and dried. Evaporation of the methylene chloride left a clear liquid which was shown by vpc to be pure *exo*-norbornyl bromide. From the relative integral values of the nmr spectrum (C_6H_6) at δ 3.70 (C-2 H), 2.33 (C-1 H), and 0.54–2.25 ppm (remainder of H), the product ratio was determined (Table I). A sample of the product was placed back under the reaction conditions for an additional 75 min and then recovered and analyzed by nmr. No significant change in the spectrum or relative integral values was observed. Vpc analysis on the Zonyl E-7 column at 95° and a helium flow of 85 ml/min showed only exo product.

Addition of 48% Hydrobromic Acid to 1.[19]—To 3.3 g (0.0196 mol) of 48% hydrobromic acid was added 1.22 g (0.0127 mol) of **1**, and the mixture was heated to 60° for 3 hr. The mixture was then cooled and the organic portion was separated. The aqueous layer was extracted with three portions of ether and the organic portions were combined. The organic phase was washed with water until neutral to litmus and was then dried. Distillation afforded 0.574 g (27%) of material, bp 68–70° (15 mm) [lit.[35] undeuterated bp 80° (28 mm)]. Vpc analysis with the Zonyl E-7 column showed only exo isomer was present. From the nmr spectrum (C_6H_6) of the sample the product ratio was determined (Table I).

Addition of Hydrogen Fluoride to 1.—To a polyethylene container cooled to −78° was added 10 ml of methylene chloride, and 1 ml of liquid hydrogen fluoride was condensed into it. A solution of 0.940 g (0.01 mol) of **1** in 5 ml of methylene chloride was added. The reaction mixture was stirred vigorously for 5 min at −78°, then quenched with enough 7–10% sodium bicarbonate solution to neutralize the excess acid present. The or-

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[28] H. C. Brown and J. H. Kawakami, *J. Amer. Chem. Soc.*, **92**, 201 (1970).

[29] Nmr spectra were recorded with a Varian A-60 spectrometer (see Table I footnote). Vpc analyses were performed with the appropriate column on a Varian Associates Model 1520-C or Model 200 gas chromatograph. Mass spectra were obtained with a Hitachi RMU-6 mass spectrometer.

[30] N. A. LeBel, *ibid.*, **82**, 623 (1960).

[31] L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 757.

[32] H. C. Brown and M. H. Rei, *J. Org. Chem.*, **31**, 1090 (1966).

[33] F. M. Sonnenberg, Ph.D. Thesis, University of Iowa, 1966, p 86.

[34] J. D. Roberts and W. Bennett, *J. Amer. Chem. Soc.*, **76**, 4623 (1954).

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

ganic portion was collected and dried. Evaporation of the solvent and sublimation of the residue afforded 0.171 g (15%) of *exo*-norbornyl fluoride. Norbornene telomers (0.291 g) were also isolated. The *exo*-norbornyl fluoride obtained was further purified by preparative vpc on the 15% SE-30 column at 70° with a helium flow rate of 85 ml/min. The nmr spectrum of the purified material was virtually identical with that of an authentic sample of *exo*-norbornyl fluoride.[20] The product ratio was determined from the nmr spectrum ($CDCl_3$) (Table I). The relative integrals at δ 4.55 (C-2 H, J_{HF} = 56.5 Hz), 2.05–2.62 (C-1 and C-4 H), and 0.67–2.05 (remainder of H) were measured. Mass spectral analysis showed the material to be greater than 95% d_2 isomer.

Addition of Formic Acid to 1. Boron Trifluoride Catalyzed Addition.—To a solution of 2 ml (0.054 mol) of formic acid, 1 ml of boron trifluoride etherate, and 50 ml of methylene chloride at −22° (tetrachloroethylene slush bath) was added 0.832 g (0.0087 mol) of **1** in 4 ml of methylene chloride. The reaction mixture was stirred at −22° for 60 min and then poured onto enough 7–10% sodium bicarbonate solution to neutralize all of the acid present. The organic portion was collected and dried; the solvent was removed to yield 0.818 g (66%) of clear liquid. Vpc analysis with a 20% SE-30 (5 ft by $^1/_4$ in.) column at 125° and a helium flow of 70 ml/min showed the product to be *exo*-norbornyl formate. A sample of a mixture of *exo*- and *endo*-norbornyl formates could be separated on this column under these conditions. The nmr spectrum ($CDCl_3$) of the formate product was recorded and the amounts of exo–cis addition, Wagner–Meerwein rearrangement, and 6,2-hydride shift were determined (Table I). The relative integrals at δ 7.96 (HCO_2), 3.70 (C-2 H), 2.14–2.47 (C-1 and C-4 H), and 0.83–2.00 (remainder of H) were measured.

Uncatalyzed Addition.—To 4.12 g (0.089 mol) of formic acid at ambient temperature was added 0.681 g (0.007 mol) of **1**. The reaction mixture was stirred for 48 hr and then poured onto dilute sodium bicarbonate solution. Work-up in the usual manner, followed by distillation, afforded 0.50 g (50%), bp 74–75° (20 mm) [lit.[36] undeuterated bp 79–80° (25 mm)], of *exo*-norbornyl formate. The nmr spectrum ($CDCl_3$) of the product was recorded and the product distribution was determined (Table I). Vpc analysis as described above showed only *exo*-formate was present.

***endo,endo*-2,3-Dideuterio-*exo*-2-norbornanol (12).**—The hydroboration of **1** was carried out exactly as described[37] with 1.995 g (0.021 mol) of **1**. After work-up and sublimation, 1.97 g (84%) of **12** was obtained. The nmr spectrum ($CDCl_3$) was similar to that of *exo*-norbornanol, except the resonance at δ 3.75 ppm (hydrogen attached to carbon bearing the alcohol group) was nearly absent in the spectrum of **12**. The integral ratio of the spectrum of **12** was consistent with the presence of two atoms of deuterium per molecule.

***endo,endo*-2,3-Dideuterio-*exo*-2-norbornyl Formate (13).**—A mixture of 0.45 g (0.004 mol) of **12** and 3 ml of formic acid was stirred for 10 hr at room temperature. The reaction mixture was quenched with dilute sodium bicarbonate solution and then the product was isolated in the usual manner. Flash distillation afforded 0.355 g (60%) of material, bp >100° (20 mm). The nmr spectrum of the product was identical with that of *exo*-norbornyl formate, except the signal at δ 4.70 ppm (hydrogen attached to the carbon bearing the formate group) was absent. The integral ratio was consistent with two atoms of deuterium per molecule.

A sample of this material was placed under the reaction conditions described for the boron trifluoride etherate catalyzed addition of formic acid to **1** for a period of 62 min. The material was recovered and its nmr spectrum ($CDCl_3$) was essentially identical with that of **13**, with no signal at δ 4.70 ppm.

Addition of Phenol to 1.—To 1.210 g (0.0126 mol) of **1**, 1.246 g (0.0132 mol) of phenol, and 25 ml of methylene chloride, cooled to −22°, was added 0.25 ml of boron trifluoride etherate. After 4 hr the mixture was quenched with 10% sodium hydroxide solution. The aqueous portion was extracted several times with methylene chloride and the extract was dried. Evaporation of the methylene chloride and distillation of the residual liquid afforded 0.891 g (41%) of material, bp 78–80° (0.3 mm). Vpc analysis on the 15% SE-30 column showed only one component. The nmr spectrum ($CDCl_3$) of the product was consistent with that expected for *exo*-norbornyl phenoxide. The relative integrals at δ 6.61–7.50 (OC_6H_5), 4.10 (C-2 H), 2.10–2.99 (C-1 and C-4 H), and 0.83–2.00 ppm (remainder of H) were measured and the product ratio was determined (Table I).

Anal. Calcd for $C_{13}H_{14}D_2O$: C, 82.06; H and D, 9.53. Found: C, 82.07; H and D, 9.60.

Addition of Methanol to 1.—To a mixture of 20 ml of methanol and 1.18 ml of sulfuric acid at the reflux temperature was added 1.445 g (0.015 mol) of **1** in 3.6 ml of methanol. The mixture was heated at the reflux temperature for 21.5 hr and then poured onto enough sodium bicarbonate solution to neutralize the acid present. The product was extracted with ether, and distillation of the dried ether extracts afforded 1.033 g (56%), bp 84° (85 mm) [lit.[38] undeuterated bp 56–62° (30 mm)], of *exo*-norbornyl methoxide. Vpc analysis on a 20% SE-30 (5 ft by $^1/_4$ in.) on Chromosorb W column at 125° with a helium flow rate of 60 ml/min showed only exo isomer was present. The exo and endo isomers could be separated by this column under these conditions. From the nmr spectrum ($CDCl_3$) the product ratio was determined (Table I) by measurement of the relative integrals at δ 3.17 (C-2 H and OCH_3), 2.00–2.30 (C-1 and C-4 H), and 0.75–1.80 ppm (remainder of H).

Registry No.—**1**, 13317-75-4; **15**, 26854-01-3; hydrogen chloride, 7647-01-0; hydrogen bromide, 10035-10-6; hydrogen fluoride, 7664-39-3; formic acid, 64-18-6; phenol, 108-95-2; methanol, 67-56-1.

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