Acid-Catalyzed Rearrangements of the Pinyl System[1]

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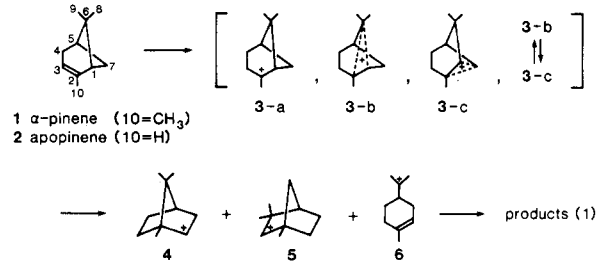
The additions and rearrangements of α-pinene (1) and apopinene (2) in deuteriated acids have been studied. The results obtained for 1 suggest that one of the reaction paths involves the tertiary cation intermediate **3a**, but it has been difficult to define clearly the stereoelectronic relation between additions and rearrangements in this system. However, in the case of deuterium addition to **2**, the stereospecific deuterium location at C-6-endo in the product **7**, the considerable preference for sterically hindered exo-side addition, and the rate enhancement of 48 times for CF_3COOH addition to **2** compared with cyclohexene are interpreted to mean that the additions are assisted by concerted C-6–C-1 or C-7–C-1 bond migration corresponding to endo- and exo-side addition, respectively. Furthermore in β-fenchoisocamphorol (**9**) obtained in CF_3COOD addition to **2**, the fraction of deuterium at C-1 (0.40) exceeds that at C-2-endo (0.36) as shown in the ^2H NMR spectrum. The same result is observed in **9** from model compounds **17** and **18**. These facts are interpreted as resulting either from an equilibrium between the cation intermediates I and II, in which II is favored due to the secondary α-deuterium isotope effect on I, or from an isotopic perturbation of resonance in a bridged structure, which favors product formation with deuterium at C-1.

Electrophilic additions of protonic acids to α-pinene (1) have been intensively investigated due to the chemical interest in the complexity of the reaction[2] and also due to the industrial importance of the rearranged products.[2p] In general, protonation of α-pinene initiates rearrangements to give three types of products: (i) camphane derivatives from cation **4** formed by C-6–C-1 migration in **1**, (ii) fenchane derivatives from cation **5** formed by C-7–C-1 migration in **1**, and (iii) monocyclic *p*-menthane derivatives from cation **6** formed by C-6–C-1 fission in **1** (eq 1).



However, the lack of information about the initial protonation, which is a key step relating to either subsequent or simultaneous rearrangements, makes the understanding of factors controlling the reaction more difficult. This is typically shown in the variety of structures proposed for the first formed cation intermediates, which have been depicted as taking either the form of **3a**,[2b,c] a pair of forms **3b** and **3c**,[2f,g] or in some cases an equilibrium between **3b** and **3c**[2j,k] (eq 1).

From the structural point of view, α-pinene and apopinene (**2**) have a Y-shaped structure with equivalent steric requirements[3] in both the exo and endo sides, except for the 6,6-dimethyl substituents. This distinctive structural character is advantageous for the study of addition mechanisms of bridged bicyclic systems[4] due to the freedom from considerations of torsional effects,[5] nonequivalent orbital extension,[6] and staggering effects.[7] The first object of this study is to clarify whether or not stereoelectronic controls are observed during additions and rearrangements in this system. Protonation assisted by concerted rearrangements requires proper stereoelectronic orientation, but this is not the case for assistance by strain relief. The second object is to determine the pathways

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(1) A part of this work was presented at the 7th IUPAC Conference on Physical Organic Chemistry at Auckland in 1984. The names used for the compounds in this paper correspond to the approved names written below: α-pinene, 2,6,6-trimethylbicyclo[3.1.1]hept-2-ene; β-pinene, 6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane; camphane, 1,7,7-trimethylbicyclo[2.2.1]heptane; fenchane, 1,3,3-trimethylbicyclo[2.2.1]-heptane; *p*-menthane, 1-methyl-4-(1-methylethyl)-cyclohexane; apopinene, 6,6-dimethylbicyclo[3.1.1]hept-2-ene; α-fenchol, 1,3,3-trimethylbicyclo[2.2.1]heptan-2-*endo*-ol; α-isofenchol, 1,5,5-trimethylbicyclo-[2.2.1]heptan-2-*exo*-ol; α-terpinenylacetate, α,α,4-trimethyl-3-cyclohexene-1-methylacetate; limonene, 1-methyl-4-(1-methylethenyl)cyclohexene; α-nopinol, 6,6-dimethylbicyclo[3.1.1]heptan-2-*exo*-ol; β-nopinol, 6,6-dimethylbicyclo[3.1.1]heptan-2-*endo*-ol; nopinone, 6,6-dimethylbicyclo[3.1.1]heptan-2-one; isonopinone, 6,6-dimethylbicyclo[3.1.1]heptan-3-one; β-fenchoisocamphorol, 5,5-dimethylbicyclo[2.2.1]heptan-2-*exo*-ol; camphenilone, 3,3-dimethylbicyclo[2.2.1]heptan-2-one; apocyclene, 3,3-dimethyltricyclo[2.2.1.$0^{2,6}$]heptane; *endo*-camphenilol, 3,3-dimethylbicyclo[2.2.1]heptan-2-*endo*-ol; *exo*-camphenilol, 3,3-dimethylbicyclo-[2.2.1]heptan-2-*exo*-ol; β-fenchocamphorone, 5,5-dimethylbicyclo[2.2.1]-heptan-2-one; camphene, 2,2-dimethyl-3-methylenebicyclo[2.2.1]heptane; α-santenol, 1,*anti*-7-dimethylbicyclo[2.2.1]heptan-2-*exo*-ol.

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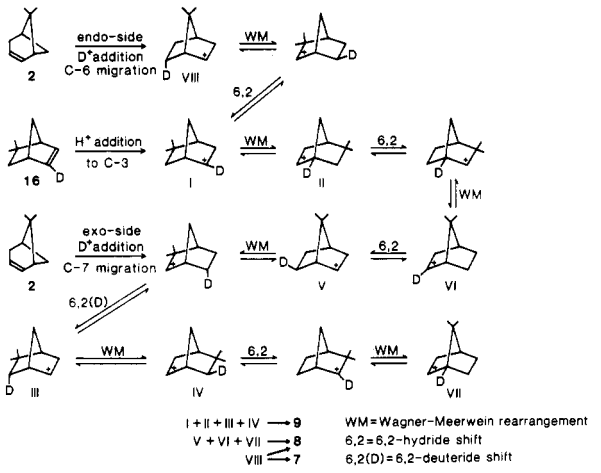
Table I. Deuterium Contents[a] in Products from α-Pinene (1)

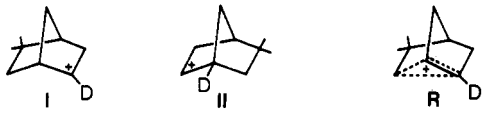
	borenol (4a)		isoborneol (4b)		α-fenchol (5a)		
position[b]	B	C	B	C	B	C	α-isofenchol (5b): B
2x	0.00	0.00			0.00	0.00	
2n			0.04	0.00			0.65
3x	0.00	0.00	0.04	0.00			0.06
3n	0.00	0.00	0.28	0.16			0.06
4	0.00	0.00	0.08	0.00	0.00	0.00	0.00
5x		0.04	0.08	0.00	0.00	0.00	
5n	0.08[c]		0.08	0.00	0.00	0.00	
6x		0.03	0.19	0.06	0.70	0.90	0.08
6n	0.80	0.90	0.19	0.52	0.06	0.18	0.08
7s					0.00	0.00	0.49
7a					0.00	0.00	0.45
8-Me	0.06	0.00	1.00	0.30	0.00	0.00	0.04[d]
9-Me	0.08	0.00	1.03	0.09	0.00	0.00	
10-Me	0.12	0.21	0.94	1.00	0.09	0.34	1.38

[a] Determined by integrated signal-intensity of $Eu(dpm)_3$-shifted 30.710-MHz ^2H NMR spectra. The largest value obtained from ^2H NMR spectra in each product was made equal to that obtained from ^1H NMR spectra on a Varian HA-100.[2o] The accuracy for the number of ^2H atoms at each position is 0.05. B: in AcOD–B_2O_3 at 130 °C for 24 h. C: in AcOD at 130 °C for 24 h. [b] X, n, s, and a denote exo, endo, syn, and anti, respectively. [c] Total values at 5x, 5n, and 6x. [d] Total values at 8-Me and 9-Me.

Scheme I. Pathways to Intermediates from 2 and 16



involving capture of cationic intermediates after initial protonation. For these objectives, as described below, α-pinene was found to be an unsuitable substrate while apopinene satisfactorily met the requirements by giving a secondary carbocation demanding more assistance for its formation than the tertiary ion in the case of α-pinene. In addition, the structures I and II, which are either canonical resonance structures of a bridged ion, R, or rapidly interconverting cation intermediates (Scheme I) formed by CF_3COOD addition to **2**, are identical except for the deuterium at C-2 in I and at C-1 in II. This gives the



advantage of using a single deuterium and racemic precursors in the elucidation of the structures of the cation intermediates.

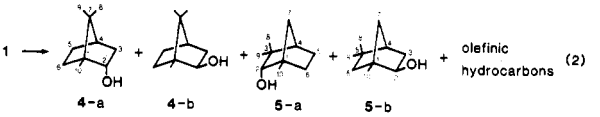
Our previous report[2o] on the deuterium distribution in products obtained in the CH_3COOD addition to α-pinene had the drawback of low accuracy in the deuterium analysis, which attempted to circumvent the inevitable inaccuracy in measuring the decrease of the integrated peak area in ^1H NMR spectral analysis. In the current study, we present interesting results obtained by ^2H NMR analysis of deuterium distributions in the products from deuteriated acid addition to **1**, **2**, and related model compounds (**16–18**) and also some kinetic data for addition reactions, all of which are interpreted by the concept of anchimeric assistance[8,9] by a migrating bond in the transition state of the initial rate-determining protonation.

16 **17** **18**

These results also indicate the possibility of either the rapidly interconverting intermediates I and II or the bridged intermediate R[10] for the free cation intermediates before solvent capture.

Results

Deuteriated Acetic Acid Addition to α-Pinene (1). Compound **1** was heated in AcOD (15 molar equiv of AcOD and 1 molar equiv of B_2O_3)[2o,11] at 130 °C for 24 h, procedure B. Gas chromatographic (GC) analysis of the products obtained after hydrolysis of the resulting acetates showed the deuteriated alcohols borneol (**4a**), isoborneol (**4b**), α-fenchol (**5a**), α-isofenchol (**5b**), and a mixture of olefinic hydrocarbons in the ratio of 20%, 25%, 20%, 10%, and 25%, respectively (eq 2). Compound **5b** was not



found in the products obtained in AcOD (15 molar equiv) at 130 °C for 24 h, procedure C. Corresponding AcOH–B_2O_3 addition to **1** gave nondeuteriated alcohols **4a**, **4b**, **5a**, and **5b**, which were identified by spectral comparison with authentic samples.[12] Control experiments showed

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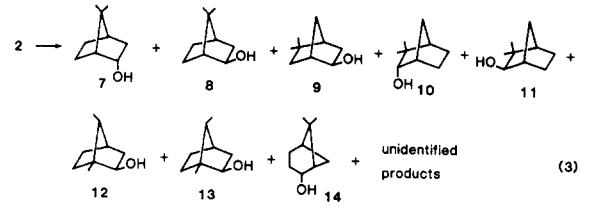
that the acetates of alcohols **4a–5b** were unchanged under the conditions of the addition reaction, but α-terpinenyl acetate was found to change to limonene under these conditions. Deuterium content at each position in **4a–5b** was determined by signal integration of $Eu(dpm)_3$-shifted **2H** NMR spectra[21] (Table I). The results are summarized by four features: (i) in endo-directed alcohols **4a** and **5a**, the distributions are simple (for example, in method C, 0.90 deuterium is found at C-6-endo in **4a** and 0.90 deuterium is found at C-6-exo in **5a**, both of which are close to unity); (ii) in exo-directed alcohols **4b** and **5b**, the deuterium is found to be scrambled to a much greater extent; (iii) in **5a** a substantial amount of deuterium is located at C-6-endo (0.18); (iv) both endo-directed alcohols, **4a** and **5a**, contain a significant amount of deuterium at the 10-methyl position (0.21 in **4a** and 0.34 in **5a** in procedure C).

Feature iv is illustrated by the ^{13}C NMR spectral region containing C-1 in **4a**, which reveals the presence of CH_2D, CHD_2, and CD_3 in the 10-methyl group (Figure 5 in the supplementary material).

Addition of Deuteriated Acids to Apopinene and Model Compounds. Apopinene synthesis[13] by the pyrolysis of α-nopinol (**15**) or β-nopinol (**14**) in the presence of $KHSO_4$ was found to give apocyclene and *endo*-camphenilol (**10**) as major products.[2i] The synthesis from nopinone obtained by ozonolysis of β-pinene followed by a Bamford–Stevens reaction[14] of the nopinone tosylhydrazone in *N,N,N′,N′*-tetramethylethylenediamine[15] gave apopinene (bp 142–143 °C) [lit.[16] bp 140.5 °C], which showed ^1H and ^{13}C NMR spectra identical with reported data.[3]

Addition of CF_3COOD or CF_3COOH to **2** at 0 °C for 40 min, followed by alkaline hydrolysis, gave apoborneol (**7**), apoisoborneol (**8**), β-fenchoisocamphorol (**9**), *endo*-camphenilol (**10**), *exo*-camphenilol (**11**), α-santenol (**12**), 1,*syn*-7-dimethylbicyclo[2.2.1]heptan-2-*exo*-ol (**13**), β-nopinol (**14**), unidentified alcohols, and a small amount of unidentified hydrocarbons in the ratio of 18.5%, 12.9%, 43.2%, 0.7%, 2.5%, 5.1%, 2.8%, 1.1%, 6.9% and 6.2%, respectively (60% yield), whose GC analysis is shown in Figure 1 (eq 3). The relative peak areas of **7–11** and **14**



(3)

remained almost constant for reaction times between 0.5 and 50 min, but peaks due to **12** and **13** showed gradual increases, while unidentified peaks (labeled as u in Figure 1) showed gradual decreases.

Table II. Deuterium Contents[a] in Products from Apopinene (2)

position	apoborneol (7)[b,c]	apoisoborneol (8)[b]	β-fenchoisocamphorol (9)[b]
2n	0.000	0.168	0.354
1	0.000	0.086	0.404
6x	0.000	0.178	0.118
6n	1.000	0.568	0.124

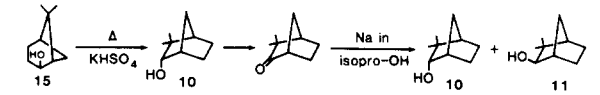
[a] Normalized values determined by 30.710-MHz ^2H NMR spectroscopy with an accuracy of 0.01 ^2H atom. [b] Reaction conditions: in CF_3COOD at 0 °C for 40 min. [c] Reaction conditions: in [$DClO_4$ (0.6)–AcOD (66.2)–D_2O (33.2), % w/w] at 105 °C for 40 h.

Table III. Deuterium Contents[a] in β-Fenchoisocamphorol (9) from Apopinene (2) and Model Compounds 16–18

	substr			
position	2[b,d]	16[c,e]	17[c,e]	18[b,e]
2n	0.387	0.498	0.187	0.282
1	0.366	0.409	0.197	0.292
6x	0.120	0.045	0.088	0.171
6n	0.127	0.048	0.085	0.171
7s	0.000	0.000	0.236	0.021
3x	0.000	0.000	0.207	0.021
7a	0.000	0.000	0.000	0.021
3n	0.000	0.000	0.000	0.021

[a] Normalized values determined by ^2H NMR spectroscopy. [b] Obtained at 61.396 MHz with an accuracy of 0.005 ^2H atoms. [c] Obtained at 30.710 MHz with an accuracy of 0.01 ^2H atom. [d] Reaction conditions: in [$DClO_4$ (0.6)–AcOD (66.2)–D_2O (33.2), % w/w] at 105 °C for 40 h. [e] Reaction conditions: in CF_3COOH at 0 °C for 40 min.

Apoborneol (**7**), apoisoborneol (**8**), and β-fenchoisocamphorol (**9**) from **2** were isolated by silica gel chromatography and identified by agreement of the NMR spectral data (Table V, supplementary material) with those of authentic samples derived from separate routes as described in the experimental section of the supplementary material. The assignments of the alcohols **10–13** were carried out by GC analysis, with authentic samples prepared according to the routes of eq 4[17] and eq 5. Alcohol



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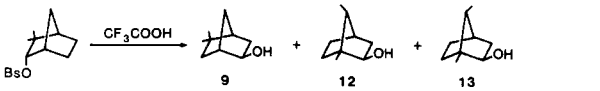

(5)

13 was differentiated from **12** by the presence of long-range coupling in the ^1H NMR spectrum between the C-2-endo proton and the C-7-anti proton ($^4J_{2n,7a}$ = 1.3 Hz) and between the C-3-endo proton and the C-7-anti proton ($^4J_{3n,7a}$ = 1.0 Hz) (Table V).

The structure of the alcohol corresponding to the small GC peak (a in Figure 1), which has the same retention time as authentic β-nopinol (**14**; eq 9), was confirmed by the agreement of its mass fragmentation pattern with that of the authentic alcohol **14** (Figure 6 in the supplementary material). α-Nopinol (**15**; eq 4) and β-isonopinol (**19**; eq 9), which have retained configurations, could not be detected in any fractions eluted from silica gel chromatography of the products.

The characteristic deuterium distribution in **7** and **9**, as described in the deuterium incorporation features 1 and 3 below, was found to be unchanged between the early (10 min) and the late (40 min) products from CF_3COOD addition to **2**. The addition of the much more nucleophilic

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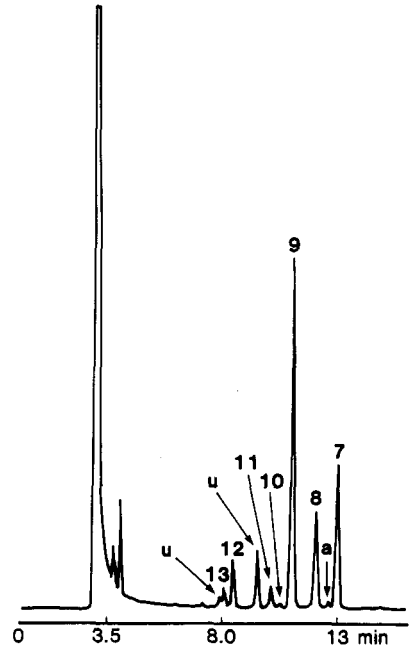
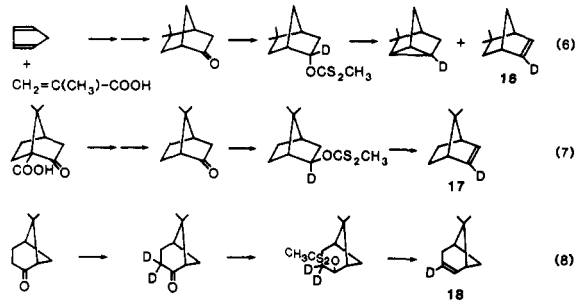


Figure 1. Chromatograms of products obtained from CF_3COOH addition to **2**, separated on a Carbowax 20 M silica gel capillary column (25 m × 0.2 mm) at 110 °C; u denotes the peaks of unidentified products; a ≡ **14**, see Figure 6 in supplementary material.

solvent[4k,n] ($DClO_4$ (0.6)–AcOD (66.2)–D_2O (33.2), % w/w) to **2** was carried out at 105 °C for 40 h, and the deuterium distribution in **7** and **9** was compared with that obtained by CF_3COOD addition (Tables II and III).

In order to characterize the intermediates I, II, III, and IV in Scheme I, which lead to **9** with deuterium substitution at C-2-endo, C-1, C-6-endo, and the C-6-exo positions, respectively, three model compounds, 5,5-dimethyl-2-deuterio-2-norbornene (**16**), 7,7-dimethyl-2-deuterio-2-norbornene (**17**), and 3-deuterioapopinene (**18**) were synthesized through pyrolysis of the corresponding xanthates[18] derived from β-fenchocamphorone,[19,50,51] ketopinic acid,[18,20] and 3,3-dideuterionopinone,[21] respectively (eq 6, 7, and 8). The deuterium distribution in **9** from CF_3COOH addition is reported in Table III.



Deuterium Distribution. The deuterium content in each position of the alcohols **7–9**, obtained in CF_3COOD addition to **2**, and of the alcohol **9**, obtained in CF_3COOH addition to model compounds **16**, **17**, and **18**, was determined by integrated signal-intensity measurements of ^2H NMR spectra. The results listed in Tables II and III are characterized by four features: (1) only one deuterium is incorporated at C-6-endo in **7**, obtained both from CF_3COOD addition or from $DClO_4$–AcOD–D_2O addition to **2**; (2) in **8**, obtained from CF_3COOD addition to **2**, deuteriums are scrambled to C-6-endo, C-6-exo, 2-endo, and also to C-1; (3) in **9**, obtained from CF_3COOD addition to **2**, the fraction of deuterium at C-1 was slightly greater than

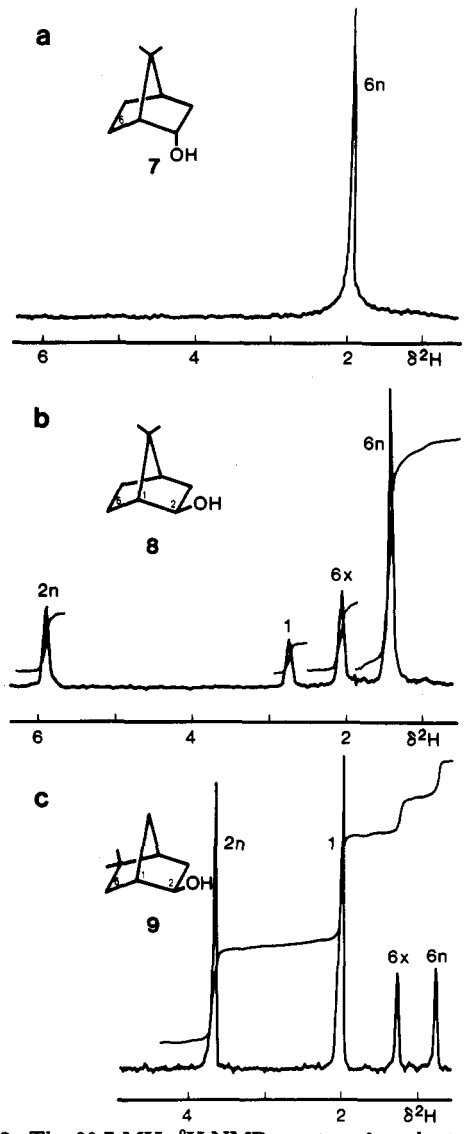


Figure 2. The 30.7-MHz ^2H NMR spectra of products obtained from CF_3COOD addition to **2**: a, apoborneol (**7**) in $CHCl_3$; b, apoisoborneol (**8**) in $CHCl_3$ containing $Eu(dpm)_3$; c, β-fenchoisocamphorol (**9**) in $CHCl_3$.

that at C-2-endo; (4) opposite results to the above (deuterium at C-1/deuterium at C-2-endo < 1) were observed in the cases of CF_3COOH addition to **16** and $DClO_4$–AcOD–D_2O addition to **2**. Figure 2 shows the 30.7-MHz ^2H NMR spectra of **7–9**, which were obtained from CF_3COOD addition to **2**. Figure 3 shows the 30.7-MHz ^2H NMR spectra of **9** obtained from CF_3COOH addition to **16** and $DClO_4$–AcOD–D_2O addition to **2**. Figure 4 shows the ^1H NMR spectrum of **9**, obtained from CF_3COOD addition to **2**, which confirmed the ratio (1.1) of the deuterium at C-1 to that at C-2-endo in **9**, shown in Figure 2.

Kinetic Results. In Table IV are listed pseudo-first-order rate constants for addition of CF_3COOH to **2** and to cyclohexene at 0 °C, which were determined by using n-$C_{10}H_{22}$ as an internal reference in the gas chromatographic analysis of the remaining alkenes in the addition reaction solutions. The rate ratio at 0 °C ($k_{apopinene}/k_{cyclohexene}$ = 48.4) indicates a moderate rate enhancement for **2**. The relative rate ratio of norbornene vs **2** (13.1) in competitive CF_3COOH addition at 0 °C was determined by the Ingold–Shaw equation,[22] and the results were obtained from GC analysis of the remaining alkenes, with

(22) Ingold, C. K.; Shaw, F. R. *J. Chem. Soc.* **1927**, 2918–2926.

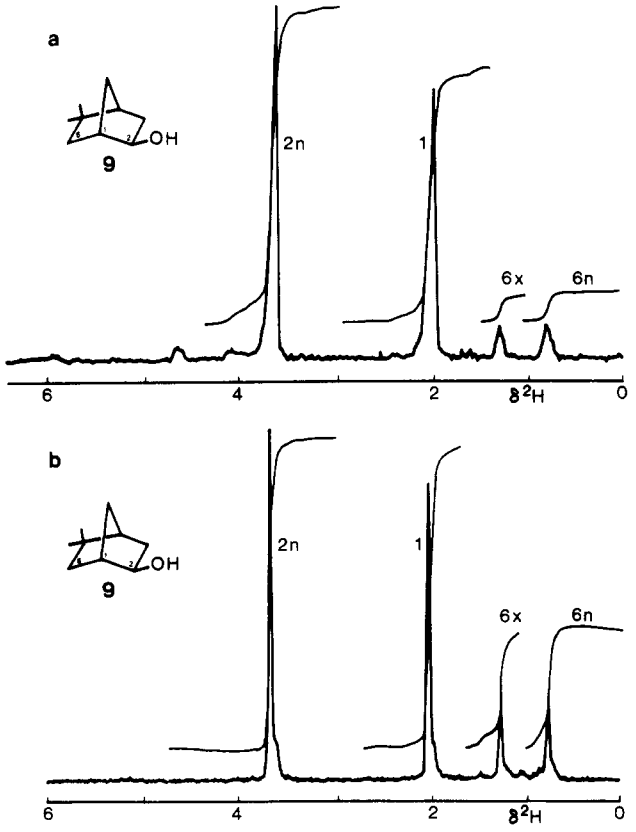


Figure 3. The 30.7-MHz ^2H NMR spectra of β-fenchoisocamphorol (**9**) in $CHCl_3$ addition to **2**: a, **9** obtained in CF_3COOH addition to **16**; b, **9** obtained in $DClO_4$ (0.6)–AcOD (66.2)–D_2O (33.2), % w/w.

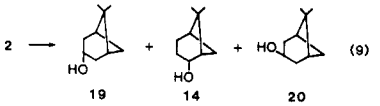
Table IV. Kinetic Data[a] Obtained in Addition Reactions to 2 and Reference Compounds

substr	reactn condtn[h]	rate constant × 10^5 s^{-1}	rel rate
2[b]	A	149	48.4
cyclohexene[c]	A	3.08	1.0
2[d]	B		1.0
norbornene[e]	B		13.1
2[f]	C		1.0
cyclohexene[g]	C		1.61

[a] Obtained by GC analysis with an internal standard compound. [b] Apopinene, 0.142 M; n-$C_{10}H_{22}$, 0.0353 M. [c] Cyclohexene, 0.0571 M; n-C_9H_{20}, 0.0140 M. [d] Apopinene, 0.0110 M; n-$C_{12}H_{26}$, 0.0150 M. [e] Norbornene, 0.2001 M; n-$C_{12}H_{26}$, 0.0150 M. [f] Apopinene, 0.0873 M; n-$C_{12}H_{26}$, 0.0176 M. [g] Cyclohexene, 0.552 M; n-$C_{12}H_{26}$, 0.0176 M. [h] A: CF_3COOH addition at 0 °C. B: Competitive addition of CF_3COOH at 0 °C. C: Competitive addition of $BH_3(CH_3)_2S$ in CH_2Cl_2 at 0 °C.

n-$C_{12}H_{26}$ as an internal reference (Table IV). The same treatment in competitive hydroboration of cyclohexene and **2** at 0 °C in CH_2Cl_2 yielded the rate ratio of $k_{cyclohexene}/k_{apopinene} = 1.61$ (Table IV).

BH_3 Addition to 2. Hydroboration of **2** with borane–dimethyl sulfide complex[23] in n-hexane at room temperature for 4 h and oxidation by alkaline hydroperoxide gave β-isonopinol (**19**), β-nopinol (**14**), and α-isonopinol (**20**) in the ratio of 86:12:2, respectively, as determined by GC analysis (eq 9). Silica gel chromatography of the product



(23) Lane, C. F. *J. Org. Chem.* **1974**, *39*, 1437–1438.

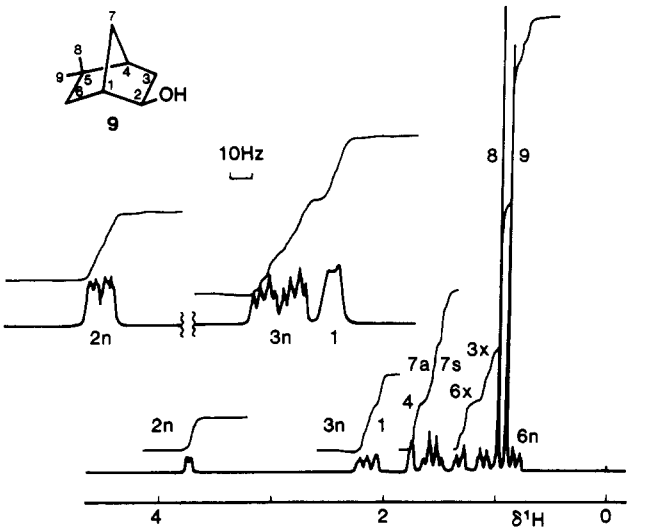


Figure 4. The 200-MHz ^1H NMR spectrum of β-fenchoisocamphorol (**9**) in $CDCl_3$ obtained from CF_3COOD addition to **2**.

alcohols gave **19** (mp 47–48 °C) [lit.[24] mp 45 °C] and **14** as a glistening soft solid [lit.[24] mp 37 °C]. ^1H NMR spectra of both alcohols agreed with the reported data.[24] Oxidation of **19** with CrO_3–pyridine afforded isonopinone, which gave the (2,4-dinitrophenyl)hydrazone (mp 161.5–162 °C) [lit.[24] mp 162 °C]. The above treatment with **14** gave a ketone that showed the same IR spectrum as that of nopinone. Compound **20** was assigned as α-isonopinol from GC analysis, by using an authentic sample prepared from $LiAlH_4$ reduction of isonopinone.

Discussion

Addition to α-Pinene. It has been reported that the addition of HCl to α-pinene under special conditions affords a very unstable pinene hydrochloride.[2a,25a] Recently, the structure of pinene hydrochloride was assigned as **22** by direct ^{13}C and ^2H NMR spectral analysis of the reaction solution.[25b] These results, along with the deuterium ac-

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cumulation at the 10-methyl position in products in this study (feature iv), suggest the intervention of the tertiary cation intermediate **3a** (eq 1). The intermediate **3a** is presumably generated both from endo-side and from exo-side deuteration and, in general, undergoes rearrangements to give one of the next intermediates **4**–**6** by the processes noted earlier or to give β- or α-pinene by H^+ elimination. As already reported,[2i-k] the formation of β-pinene, which was observed at the beginning of the reaction of α-pinene, gives supporting evidence for the presence of the intermediate **3a**.

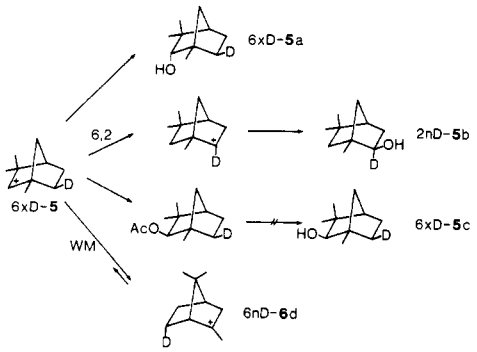
The high deuterium content at C-6-endo in **4a** and at C-6-exo in **5a** (feature i in the endo products) is interpreted to mean that the initial deuteriation occurs from the less hindered endo side to give **3a** followed by two kinds of bond migrations, namely, C-6–C-1 leading to **4** and C-7–C-1

(24) Baretta, A. J.; Jefford, C. W.; Waegell, B. *Bull. Soc. Chim. Fr.* **1970**, 3985–3993.

(25) (a) Hughes, E. D. *Q. Rev., Chem. Soc.* **1951**, *5*, 245–269. (b) Weigand, E. F.; Schneider, H.-J. *Chem. Ber.* **1979**, *112*, 3031–3033.

leading to **5**. The formation of **4** and **5** would then be controlled mainly by the migratory aptitudes[26] of C-6 and C-7, respectively. The contrasting deuterium distribution in exo products **4b** and **5b** (feature ii) may be understood by postulating a series of steps, including Wagner–Meerwein, Nametkin, 6,2- and 3,2-hydride shifts, and also H^+ elimination and D^+ addition.

The large amount, 0.65, of C-2-endo deuterium in **5b** and the absence of any 6-*exo*-deuterio-1,3,3-trimethylbicyclo-[2.2.1]heptan-*exo*-2-ol, 6xD-**5c**, are interesting. The expected products from the intermediate 6xD-**5** derived from endo-side addition followed by C-7–C-1 migration are 6-*exo*-deuterio-α-fenchol, 6xD-**5a**, 2-*endo*-deuterio-α-$\leq$-isofenchol, 2nD-**5b**, and 6-*exo*-deuterio-1,3,3-trimethylbicyclo[2.2.1]heptan-2-*exo*-ol, 6xD-**5c**, two of which, 6xD-**5a** and 2nD-**5b**, are actually obtained. The absence of 6xD-**5c** may be due to the high reactivity of the transitory *exo*-acetate, which undergoes solvolysis very rapidly to a tertiary cation intermediate, 6nD-**6d**, through Wagner–Meerwein rearrangement under the reaction conditions used.



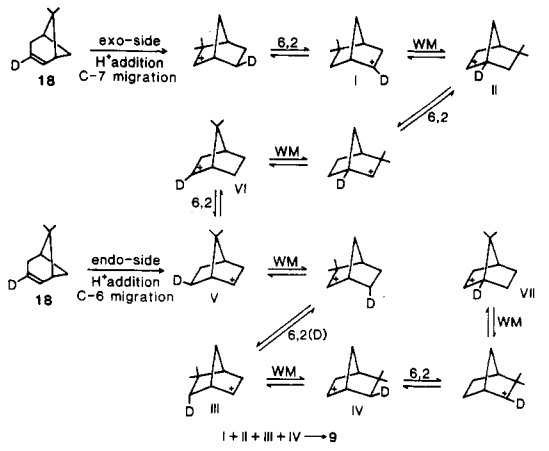
The substantial amount of deuterium at C-6-endo (0.18) in **5a** (feature iii) may be rationalized by assuming a concurrent path initiated by exo-side deuteration and assisted by C-7–C-1 bond migration to give **3c**, followed by immediate solvent capture.[4n] This interpretation provides a rationale that the steric hindrance of the *syn*-9-methyl is compensated by stereoelectronically assisted bond migration.[27]

The pathways to all the above products, **4a–5b**, particularly 4-deuterioisoborneol (**4b** in procedure B) are too complex and lengthy to present here and are given in the supplemenary material (Scheme III).

Addition to Apopinene. In protonic acid addition to α-pinene, there ought to be little, if any, need of assistance to stabilize the already very stable tertiary cation intermediates. However, in the apopinene case, there should be a considerable need of assistance in the initial protonation to give secondary cation intermediates.[28]

The advantage of using apopinene, compared to α-pinene, is that it has no methyl substituent at C-2, which results in a simple deuterium distribution in the products. This was revealed especially in **7**, which contains one deuterium located only at C-6 endo (feature 1) (Table II). This significant result was realized in one step by initial endo-side deuteriation at C-3, assisted by C-6–C-1 bond migration, with direct capture of the forming cation by the

Scheme II. Pathways to Intermediates from 18



counterion located at the endo side. Alternatively, deuteriation could give **3b** as an intermediate that leads to **7**. Unassisted protonation at C-3 could also lead to the formation of **14**, and the uncaptured free cations formed would all lead to **8** and/or to further rearranged exo derivatives (Scheme I), which have been observed[2m,4f,29] previously and in this work by CF_3COOH addition to **16**. Feature 2, the additional deuterium incorporation in **8**, particularly at C-1, gives evidence for extensive alternations of Wagner–Meerwein and 6,2-hydride (deuteride) shifts in competition with the capture of each cationic site by the solvent[12a,30] (Scheme I).

As shown in Scheme I, III and IV are intermediates for deuterium incorporation at C-6-endo and at C-6-exo in **9**, respectively. Consequently, if the initial addition to **2** occurs only from the endo side, **9** obtained from **2** and from **16** should contain the same amount of deuterium at C-6. However, there is about 3 times as much deuterium incorporation at C-6 in **9** from **2** as from **16** (Table II, III), indicating a shorter route to the intermediates III and IV from **2**, i.e., exo-side deuteration.

From comparison of Schemes I and II, the ratio (0.7) of deuterium at C-6 in **9** from **2** (Table III) vs that from **18** (Table IV) represents the approximate ratio of exo-side vs endo-side addition. This follows from the fact that the fraction that leaked through Wagner–Meerwein followed by a 6,2-shift to the intermediate VI in the case of exo-side D^+ addition to **2** (Scheme I) and the fraction that leaked through a 6,2-shift to the same intermediate VI in the case of endo-side H^+ addition to **18** (Scheme II) are almost equal. The significant amount of hindered exo-side protonation, compared with the result of the hydroboration of **2** (2%), is positive evidence supporting the view that the steric hindrance to exo approach in **2** is compensated by C-7–C-1 assistance in the initial exo-side addition.

About a 100-fold rate acceleration to one reaction site in protonation of **2** compared to cyclohexene is consistent with the formation of 1.1% of unrearranged **14** from **2** by a discrete unassisted pathway.[32] The driving forces that accelerate the initial rate-determining protonation[4g] come

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(27) Saunders, W. H., Jr.; Cockerill, A. F. *Mechanisms of Elimination Reactions*; Wiley: New York, 1973; Chapter 3.

(28) Streitwieser, A., Jr. *Solvolytic Displacement Reactions*; McGraw-Hill: New York, 1962; p 104.

(29) Colter, A.; Friedrich, E. C.; Holness, N. J.; Winstein, S. *J. Am. Chem. Soc.* **1965**, *87*, 378–379.

(30) (a) Berson, J. A.; McRowe, A. W.; Bergman, R. G. *J. Am. Chem. Soc.* **1967**, *89*, 2581–2589. (b) *Carbonium Ions*, Olah, G. A., Schleyer, P. v. R., Eds.; Vol. 2, Chapter 14 by J. L. Fry and G. J. Karabatsos. (c) Brouwer, D. M.; Hogeveen, H. In *Progress in Physical Organic Chemistry*; Vol. 9, p 179–240.

(31) (a) Yannoni, C. S.; Macho, V.; Myhre, P. C. *J. Am. Chem. Soc.* **1982**, *104*, 907–909. (b) *Ibid.* **1982**, *104*, 7380–7381. (c) Sorensen, T. S. *Acc. Chem. Res.* **1976**, *9*, 257–273.

(32) Brown, H. C. *The Nonclassical Ion Problem*; (comments by P. v. R. Schleyer); Plenum: New York, 1977; p 45.

from either C-6–C-1 or C-7–C-1 migration corresponding to endo-side or exo-side protonation, respectively, with release of strain energy[25,33] and stereoelectronic control.[27] However, the magnitude of rate acceleration is much smaller than the factor of about 10^5 observed in acetolysis of the *p*-bromobenzenesulfonate of **14**.[17a,34,35] This discrepancy is not understood at present but one reason could be an unfavorable stereoelectronic alignment in the transition state between the incipient vacant p orbital on C-2 and the migrating C-6–C-1 (C-7–C-1) bond. The dihedral angles between these are estimated to be 43° from molecular models, while in the case of acetolysis the angles between the cleaving C–O bond and the migrating C-6–C-1 bond are close to the optimum antiperiplanar orientation (180°).[27,36] The rate enhancement for norbornene compared with **2** (Table IV) by a factor of 13.1 may also be explained on the same grounds, i.e., a better (20°) angular orientation of the C-6–C-1 assisting bond to the vacant p orbital on C-2.

Isotope Effect on Intermediates.[37] The slightly greater deuterium content at C-1 rather than at C-2-endo in **9** obtained from CF_3COOD addition to **2** (Table II) is near to the limit of accuracy of area integration in NMR analysis. However, the validity of this result is supported by additional observations that the fraction of deuterium at C-1 and at C-2-endo in **9** obtained from **17** and **18** show the same tendency (Table III). Furthermore, the deuterium ratio (C-1/C-2-endo = 1.1) in **9** from CF_3COOD addition to **2** was also confirmed both by the smaller amount of proton incorporation at C-1 than at C-2-endo in the ^1H NMR spectrum (Figure 4) and by the ^{13}C NMR spectrum of **9** in which the intensity of the C-7 signal coupled with the deuterium at C-1 compared to the intensity of the C-3 signal coupled with the deuterium at C-2-endo was estimated to be in the ratio 1.1.

A slight excess of deuterium incorporation at C-1 over C-2-endo has previously been reported for CF_3COOD addition to nortricyclene,[38] (D_2SO_4–CD_3COOD) addition to nortricyclene,[39] and for deamination of 2-deuterio-2-*exo*-(*endo*)-norbornylamine in HNO_2.[40] Particularly interesting is the finding that the ratio of deuterium incorporation was reversed (0.75 in HCl to 1.09 in HF) by decreasing the nucleophilic character of X in HX addition to 2,3-dideuterio-2-norbornene.[41] This is the same result as obtained for **2** in this study.

Recently, the size and direction of the secondary deuterium equilibrium isotope effect in 1-(2,3-dimethylcyclopropyl)ethyl cation was measured by ^{13}C NMR spectral analysis to give 1.11 for K at 25 °C, which favored b due to the small deuterium isotope effect at the γ-position in b compared to that at the α-position in a.[42] In our case, the equilibrium constant for ([II]/[I]) would be expected to be very near to the above value (1.11) because the β-deuterium isotope effect in II is presumably very small due to the unfavorable orientation (~90°) between the bridgehead C–D bond and the vacant p orbital on C-2.[42,43] The observed 1.1 ratio of C-1/C-2-endo deuterium in **9** from **2** may be interpreted as reflecting the true equilibrium between the intermediates I and II, both of which are captured by solvent with almost equal rates. If this were the actual case, the equilibrium would favor II with a free energy difference of about 0.06 kcal/mol, which can be envisioned from the maximum activation energies of 0.2 kcal/mol deduced from the ^{13}C NMR analysis for the interconversion, if it occurs, between the 2-norbornyl cation pair.[31] On the other hand, the opposite results (C-1 < C-2-endo) obtained in **9** from **16** in CF_3COOH and from **2** in the much more nucleophilic medium[4k,n] $DClO_4$–DOAc–D_2O (Table III) indicate capture of the first-formed ion I by the solvent before full equilibration.[4e,f] In the case of **16**, an alternative explanation based on counterion control[44,45] is possible, but the formation of **9** from **2** due to the intervention of several 6,2-hydride and Wagner–Meerwein steps before final bond formation is not.

The effects of deuterium substitution at C-1 and C-2 on the kinetics of norbornyl solvolysis have been found to be multiplicative. This indicates a bridged ion structure in the transition state.[46] Similarly, isotope effects on the NMR spectra of the norbornyl cation have been interpreted in terms of a bridged intermediate.[47] These previous results support the alternative interpretation that our current observation represents the kinetic secondary deuterium isotope effect anticipated in the solvent capture of the bridged intermediate[10] R. The final choice between the two interpretations[48] must await further study.

Experimental Section

Apopinene (**2**), α-isofenchol (**5b**), *endo*-camphenilol (**10**), *exo*-camphenilol (**11**), α-santenol (**12**), 1,*syn*-7,7-dimethylbicyclo[2.2.1]heptan-2-*exo*-ol (**13**), and β-nopinol (**14**) are all known. 5,5-Dimethyl-2-deuterionorbornene (**16**), 7,7-dimethyl-2-deuterio-2-norbornene (**17**), and 3-deuterioapopinene (**18**) are deuterio derivatives of known compounds. Consequently, their preparative procedures and necessary constants (melting and boiling points) as well as spectral data (IR, ^1H NMR, and ^{13}C NMR) are described in the supplementary material. Detailed parameters for ^1H and ^{13}C NMR spectra of apoborneol (**7**), apoisoborneol (**8**), β-fenchoisocamphorol (**9**), *endo*-camphenilol (**10**), *exo*-camphenilol (**11**), α-santenol (**12**), 1,*syn*-7,7-dimethylbicyclo[2.2.1]heptan-2-*exo*-ol (**13**), and 6,6-dimethylnorbornan-2-*exo*-ol (**21**) are presented in the supplementary Table V. In

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(44) (a) Collins, C. J. *Chem. Soc. Rev.* **1975**, *4*, 251–262. (b) Bly, R. S.; Bly, R. K.; Hamilton, J. B.; Jindal, S. P. *J. Am. Chem. Soc.* **1977**, *99*, 204–216.
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(46) (a) Maskill, H. *J. Am. Chem. Soc.* **1976**, *98*, 8482–8485. (b) Reference 32 p 218.
(47) (a) Saunders, M.; Kates, M. R. *J. Am. Chem. Soc.* **1980**, *102*, 6867–6868. (b) Saunders, M.; Kates, M. R.; Walker, G. E. *Ibid.* **1981**, *103*, 4623–4624. (c) Saunders, M.; Kates, M. R. *Ibid.* **1983**, *105*, 3571–3573. (d) Kirchen, R. P.; Ranganayakulu, K.; Rauk, A.; Singh, B. P.; Sorensen, T. S. *Ibid.* **1981**, *103*, 588–596. (e) Hogeveen, H.; van Kruchten, E. M. G. A. *J. Org. Chem.* **1981**, *46*, 1350–1353.
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addition, supplementary material contains Figure 5, ^{13}C NMR spectra of C-1 regions of borneol (**4a**) obtained from AcOD addition to β-pinene, and Figure 6, the EI mass spectra of authentic β-nopinol (**14**) and of the product corresponding to the peak labeled a in Figure 1.

$^2H\{^1H\}$ NMR spectra were taken at least three times per sample with a Varian XL-400 or a XL-200 spectrometer at 61.396 or 30.710 MHz in spinning 5-mm cylindrical tubes or 10-mm spherical cells at normal probe temperature. The solvent was $CHCl_3$ with $CDCl_3$ added as internal reference. The magnetic field was shimmed on an analogue ^2H signal from $CDCl_3$ obtained by connecting the lock cable to the observation port of the probe, after which the instrument was run unlocked. ^2H spin–lattice relaxation times (T_1) of **9** were obtained by the inversion–recovery FT method. ^2H T_1 values of $^2H_1$, $^2H_{2n}$, $^2H_{6n}$, and $^2H_{6x}$ signals of **9** are 0.6, 0.6, 0.5, and 0.6 s, respectively. The following $^2H\{^1H\}$ FT measurement conditions were used to avoid saturation: spectral width, 1100 (61 MHz), 614 (31 MHz) Hz; acquisition time, 2 s; pulse flip angle, 20°; number of transients, 16 (61 MHz), 64 (31 MHz).

Gas chromatographic analyses were performed with a SHIMADZU Model GC-7AG instrument equipped with a peak area integrator, Chromatopack C-RIB, and the following columns: A, flexible capillary column (25 m × 0.2 mm) packed with Carbowax 20M (Hewlett-Packard); B, flexible capillary column (12.5 m × 0.3 mm) packed with Carbowax 20M (SHIMADZU); or C, glass column (3 m × 3 mm) packed with OV-17 2% on Chromosorb P (80–100 mesh) at N_2 flow of 50 mL/min. Liquid chromatography over silica gel was carried out under medium pressure on a prepacked column, size D (440 × 37 cm) Lichroprep Si60 (40–63 μm), E (310 × 25 cm), or F (240 × 10 cm) (LOBAR column Merck). Organic reagents were purchased commercially and used as received.

Trifluoroacetic acid was dried over P_2O_5 and distilled. Trifluoroacetic acid-*d* was prepared by the method of DePuy et al.[49] Trifluoroacetic acid-*d* for NMR spectroscopy (Merck) gave the same results as above. *n*-Pentane was distilled through a silvered vacuum jacketed distilling column (40 × 1.5 cm) and judged to be pure by GC analysis.

CF_3COOH Addition to 2. To distilled CF_3COOH (17.2 g, 0.151 mol) was added apopinene (1.10 g, 9.0 mmol) at 0 °C with stirring. Stirring was continued for 80 min at 0 °C. The red reaction mixture was poured into ice–water (300 mL) and extracted with *n*-pentane (3 × 100 mL). The combined extracts were washed with H_2O (200 mL), dried ($MgSO_4$), and concentrated through a 40 × 1.5 cm distilling column to yield an oil (ca. 2 mL), which was saponified by refluxing in a solution of 2 N NaOH (10 mL) and MeOH (10 mL) for 30 min. The reaction mixture was poured into ice–water (100 mL) and extracted with *n*-pentane (3 × 50 mL). The combined extracts were washed with H_2O, dried ($MgSO_4$), filtered, and concentrated to an oil (1.4 g) through a 20 × 1 cm distilling column at 90 °C bath. The oil (0.7 g) was separated into 21 fractions on a LOBAR E column with 4:1 *n*-pentane/ether and monitored by differential refractometer analysis (Waters Associates R403). The purity of each fraction was tested by GC analysis with capillary column A. From the fractions of 13, 17, and 20 were obtained **8** (22 mg, 0.157 mmol, 1.7%, mp 130–131°C) [lit.[29] mp 141–142.5 °C], **7** (33 mg, 0.235 mmol, 2.6%, mp 121–122 °C) [lit.[29] mp 131–132 °C], and **9** (52 mg, 0.371 mmol, 4.1%, mp 56–57 °C) [lit.[29] mp 60–61 °C], respectively. IR of **7** ($CHCl_3$): 3600, 3500–3150, 2945, 2875, 1455, 1386, 1370, 1335, 1285, 1265, 1145, 1120, 1096, 1070, 1035, 1003, 940, 860, 820 cm^{-1}. IR of **8** ($CHCl_3$): 3600, 3500–3200, 2940, 2870, 1473, 1450, 1383, 1364, 1307, 1275, 1120, 1075, 1025, 990, 952, 909, 875, 847, 820 cm^{-1}. ^1H NMR spectra of **7–9** are listed in Table V of the supplementary material.

To determine the structure of the alcohol obtained in extremely poor yields (t_R 12.59 min), another run [**2** (0.990 g)/CF_3COOH (35 mL), at 0 °C for 45 min] was carried out to give the alcohol (ca. 1 mg) eluted in the last fraction and contaminated with 15% of **9**. The mass spectrum of this alcohol (labeled as a in Figure 1) showed signals identical with those of authentic **14** (Figure 6, supplementary material).

The product alcohols from CF_3COOD addition to **2** were purified on 3× LOBAR E with 5:1 benzene/ethyl acetate and gave good separations with a smaller amount of eluant. Compound **9** for ^2H NMR spectral analysis was obtained from the combined fractions containing **9** to avoid differential elutions between the two species deuteriated at C-1 and at C-2-endo. Typically, 250 mg of **9** (1.78 mmol, 21.8%, mp 56–57 °C) was obtained from 1.0 g (8.18 mmol) of **2**.

CF_3COOH Addition to 16. To a stirred quantity of CF_3COOH (15 mL) was added **16** (150 mg, 1.211 mmol) at 0 °C, and after 40 min, the reaction mixture was worked up as described in the CF_3COOH addition to **2**. GC analysis of the concentrated oil (0.3 g) on column B at 90 °C showed four peaks, 9.13, 9.81, 10.61, and 11.36 min, with respective area ratios of 1%, 48%, 48%, and 3%, corresponding to an unidentified alcohol, **21**, **9**, and **8**, respectively. Separation of the crude products through 3× LOBAR F with 5:1 benzene/ethyl acetate gave **21** from early fractions and **9** from late fractions. ^2H NMR spectra of **21** (30.7 MHz) showed two signals [δ 1.66 ($^2H_{3n}$), 1.55 ($^2H_{7a}$)] with area ratios of 0.55 and 0.45. The ^1H NMR spectrum of undeuteriated **21** obtained from 5,5-dimethylnorbornene is shown in Table V.

CF_3COOH Addition to 17 and 18. The addition reactions were carried out according to the above procedure, and alcohol **9** was isolated from each of the product alcohols. ^2H NMR spectra of **9** from **17** and **18** are shown in Table II.

Kinetics of the Addition of CF_3COOH to Apopinene (2). To a stirred quantity of CF_3COOH (1 mL) in a glass-stoppered 16-mL test tube cooled in an ice–water bath was added 8 μL of the solution of apopinene (50 μL) and *n*-$C_{10}H_{22}$ (25 μL) through a microsyringe. After 1 min, the reaction mixture was quenched by *n*-pentane (5 mL) and cooled in a dry ice/acetone bath, followed by the addition of 5 mL of ice–water. The *n*-pentane extract obtained after shaking the product mixture was washed with 1% aqueous $NaHCO_3$ and was analyzed for remaining apopinene on column C at 40 °C for 4 min and then programmed to 100 °C at 5 °C/min. Under these conditions the retention times of apopinene and $C_{10}H_{22}$ were 8.35 and 10.65 min, respectively. The same analyses were carried out for samples with reaction times of 3, 8, 15, and 25 min. Linear least-squares pseudo-first-order kinetic analysis[4k] gave a rate constant $k_1 = 1.49 \times 10^{-3}$ s^{-1}, correlation coefficient 0.9963. In the case of cyclohexene, the same analysis was carried out for samples with reaction times of 30, 60, 90, 120, and 150 min to give a rate constant $k_1 = 3.08 \times 10^{-5}$ s^{-1}, correlation coefficient 0.9882.

Competitive Addition of CF_3COOH to Norbornene and Apopinene. To a stirred quantity of CF_3COOH (2 mL) in a glass-stoppered 16-mL test tube cooled in an ice–water bath was added a portion (45.4 mg) of the solution of norbornene (202 mg), apopinene (13.8 mg), and *n*-$C_{12}H_{26}$ (27.5 mg). After 35 s, the reaction mixture was quenched with *n*-pentane (5 mL) and cooled in a dry ice/acetone bath, followed by addition of 5 mL of ice–water. The pentane extract obtained after shaking the product mixture was washed with 1% aqueous $NaHCO_3$ and was analyzed by GC for the remaining norbornene and apopinene as described above. The ratio $k_{norbornene}/k_2 = 13.1$ was obtained according to the reported equation.[22]

Competitive Addition of $BH_3{\cdot}(CH_3)_2S$ to Apopinene and Cyclohexene. A 50-μL sample of the solution of cyclohexene (136 mg), apopinene (32 mg), and *n*-$C_{12}H_{26}$ (9.0 mg) in CH_2Cl_2 (2 mL) was added to *n*-pentane (1 mL). This was used as a reference sample. To the residual stirred solution in a glass-stoppered 16-mL test tube was added 1 mL of $BH_3{\cdot}(CH_3)_2S$ (1 M CH_2Cl_2 solution) at 0 °C. After being stirred for 180 min, the reaction mixture (50 μL) was added to the mixture of H_2O (5 mL) and *n*-pentane (2 mL) and shaken vigorously. The *n*-pentane extract was analyzed by GC for the remaining olefins as above to give a relative rate of $k_{cyclohexene}/k_2 = 1.61$.

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Registry No. (±)-**1**, 2437-95-8; (±)-**2**, 111821-60-4; (±)-**4a**, 6627-72-1; (±)-**4a** (acetate), 36386-52-4; (±)-**4b**, 24393-70-2; (±)-**4b** (acetate), 17283-45-3; (±)-**5a**, 36386-49-9; (±)-**5a** (acetate, 111821-74-0; (±)-**5b**, 111821-62-6; (±)-**5b** (acetate), 111773-53-6; (±)-**7**, 111821-63-7; (±)-**7** (ketone), 110012-74-3; (±)-**8**, 111821-64-8; (±)-**8**-2-*endo*-*d*, 111821-72-8; (±)-**8**-2-*endo*-*d* (methyl xanthate), 111773-51-4; (±)-**9**, 111821-65-9; (±)-**9** (ketone), 111821-71-7; (±)-**10**, 111821-66-0; (±)-**10** (*p*-brosylate), 111773-45-6; (±)-**10** (ketone), 52363-25-4; (±)-**11**, 111821-67-1; (±)-**12**, 111821-68-2; (±)-**13**, 111821-69-3; (±)-**14**, 70223-30-2; (±)-**14** (ketone), 30469-48-8; (±)-**14** (ketone tosylhydrazone), 111773-46-7; (±)-**14**-3,3-d_2 (ketone), 111821-73-9; (±)-**15**, 70223-29-9; (±)-**15**-3,3-d_2, 111793-88-5; (±)-**15**-3,3-d_2 (methyl xanthate), 111773-52-5; (±)-**16**, 111773-44-5; (±)-**16** (unlabeled), 82764-88-3; (±)-**17**, 111821-61-5; (±)-**18**, 111793-87-4; **19**, 29031-17-2; **19** (ketone), 4722-54-7; **20**, 29031-18-3; (±)-**21**, 111821-70-6; (±)-α-terpinenyl acetate, 10581-37-0; (±)-limonene, 7705-14-8; norbornene, 498-66-8; cyclohexene, 110-83-8; (±)-B-pinene, 23089-32-9; (±)-5,5-dimethyl-2-*exo*-deuterio-2-*endo*-norbornanol, 111773-47-8; (±)-5,5-dimethyl-2-*exo*-deuterio-2-*endo*-norbornyl methyl xanthate, 111773-48-9; (±)-deuterioapocyclene, 111773-49-0; (±)-apocyclene, 111773-50-3.

Supplementary Material Available: Preparative procedures, necessary constants, and spectral data for **2**, **5b**, and **10**–**18**; Table V showing the ^1H and ^{13}C NMR parameters of **7**–**13** and **21**; Scheme III showing pathways to products from α-pinene; Figure 5 showing ^{13}C NMR spectra of C-1 regions of borneol (**4a**); and Figure 6 showing the EI mass spectra of authentic β-nopinol (**14**) and of the product corresponding to the peak labeled a in Figure 1 (7 pages). Ordering information is given on any current masthead page.

Fluorinated Phosphoranium Salts: Syntheses and Mechanisms of Formation, Hydrolysis, and Halogenation

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Triphenylphosphine and/or tri-*n*-alkylphosphines (R = Et, Bu, Oc) react with fluorotrihalomethanes in a three-to-one ratio to produce fluorinated phosphoranium salts in excellent yields. The solvents utilized exclusively for the preparation of these ylides are methylene chloride, benzonitrile, and *o*-chlorotoluene. Hydrolysis of the fluorinated phosphoranium salts takes place under mild reaction conditions to produce an equivalent of phosphine oxide and (fluoromethyl)phosphonium salt. Halogenation of the fluorinated phosphoranium salts was shown to be an almost quantitative reaction to produce the corresponding (dihalofluoromethyl)phosphonium salt and dihalophosphorane. The mechanism of formation of fluorinated phosphoranium salt is a series of halophilic reactions similar to that of non-fluorine-containing phosphoranium salts. The hydrolysis of phosphoranium salts is explained by attack by hydroxide ion on the most positively charged phosphorus of the newly formed bis phosphonium salt; the stability of the ejected ylide is secondary to the formation of the strongest phosphorus–oxygen bond. Halogenation occurs by initial abstraction of positive halogen by the fluorinated phosphoranium salt to produce the bis phosphonium salt, followed by attack by halide ion on the phosphonium center, resulting in ejection of the more stable halofluoromethylene ylide.

Introduction

In 1961 Ramirez[2] reported the first synthesis of a phosphoranium salt. The name was coined because the molecule comprised both the phosphorane and phosphonium moieties. The synthetic sequence began with the

$$[Ph_3P^+–C^-H–P^+Ph_3]Br^-$$
1

preparation of methylene bis(triphenylphosphonium bromide) from 2 mol of triphenylphosphine and 1 mol of methylene bromide. Treatment of the bis phosphonium salt with aqueous sodium carbonate afforded the phosphoranium salt 1. Subsequent to this initial report, the syntheses of a variety of phosphoranium salts have appeared in the literature,[3-22] most of which have been prepared by the reaction of a tertiary phosphine with a halogenated methane. The general structure of phosphora-

Table I. Solvents and Solubilities

	solubilities[a]			
	$[Bu_3P^+–C^-F–P^+Bu_3]X^-$			
solvent (bp, °C)	$CFCl_3$	$CFBr_3$	Bu_3PCl_2	Bu_3PBr_2
methylene chloride (40)	S (95%)	S (92%)	S	S
benzonitrile (191)	S (94%)	S (91%)	S	IS
o-chlorotoluene (158)	S (92%)	S (91%)	S	IS
acetonitrile (82)	S (91%)	S (93%)	S	IS
dioxane (101)	S (90%)	S (89%)	S	IS

[a] ^{19}F NMR yield vs hexafluorobenzene (HFB): S = soluble; IS = insoluble—solid present which is not detected by ^{31}P NMR analysis.

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