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ACID-INDUCED REARRANGEMENT OF α-PINENE

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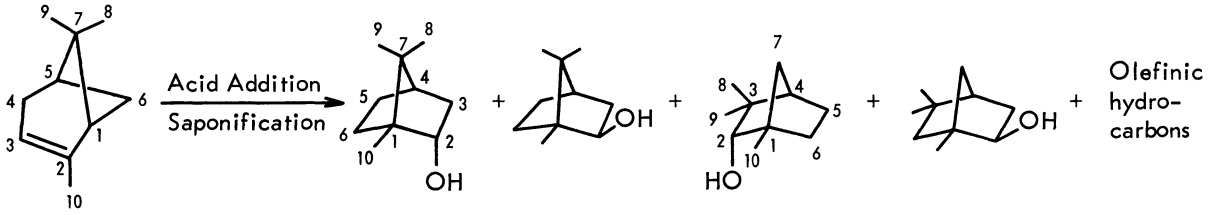
Lanthanoid-assisted ^{1}H NMR analyses of deuteriums incorporated in D^+-catalyzed rearrangement products of α-pinene showed that the pathways to the exo- (3, 5) and endo-products (2, 4) are different in nature, and that the C-1–C-6 σ-participation became involved in an electrophilic attack from the exo-side.

In bicyclo[2.2.1]heptenyl systems, it is well documented that, in stepwise electrophilic additions, electrophiles approach to the double bond from the exo-side even in the presence of the 7,7-dimethyl substituents.[1] In bicyclo[3.1.1]-heptenyl systems, however, no data indicating the sterically hindered exo-approach of electrophiles have been reported, while much information as to the endo-approach are available in cyclic molecular[2] and in stepwise electrophilic additions.[3] We report here the results which support the exo-approach by deuterium-scrambling examinations on the individual carbon sites in products obtained on AcOD addition to α-pinene.

α-Pinene (1) was treated under the following two conditions: (i) AcOD (15 molar equivalent of 1) containing B_2O_3 (1 molar equivalent of 1) at 130°C for 24 hours, and (ii) AcOD (15 molar equivalent of 1) at 130°C for 24 hours.[4] A typical example carried out under the condition (i) gave borneol (2), isoborneol (3), α-fenchol (4), β-isofenchol (5), and olefinic hydrocarbons in a ratio of 20, 25, 20, 10, and 25%, respectively, after hydrolysis of the second distilled fraction (44% yield): bp 80°-100°C (13 mm). The alcohols purified by preparative VPC and by TLC,[5] were identified by comparing their spectral data (IR and ^{1}H NMR) and VPC analyses with authentic samples obtained by the reported method.[6]

The ^{1}H NMR spectra of 2-5 in $CDCl_3$ were determined at various shift-reagent[7] [$Eu(DPM)_3$] concentrations by the procedures reported previously.[8] Because of low



1 2 3 4 5

Table I. Deuterium Content (±0.05)[a] in Each Position[b] of the Rearrangement Products Determined by $Eu(DPM)_3$-assisted ^1H NMR Spectroscopy

		2x	6n	3n	3x	10	6x	5n	5x	4	8	9
	S^c	+24.3	+16.8	+16.3	+8.5	+8.2	+8.0	+7.8	+5.0	+5.0	+4.3	+3.7
2	d	0.1_0	0.8_0	0.1_0	0.0_0		0.2_0		0.1_5[h]		0.0_0	0.0_5
	e	0.1_0	0.9_0	0.1_0	0.0_0		0.2_5[g]		0.0_0	0.0_0	0.0_0	0.0_5

		2n	3x	8	10	3n	6n	4	6x	5x	5n	9
	S^c	+23.2	+16.5	+9.6	+9.2	+8.3	+6.1	+5.2	+4.2	+4.0	+4.0	+4.0
3	d	0.0_0	0.0_0	1.0_0	1.2_0		0.2_0[h]			0.1_0		1.1_0
	e	0.0_0	0.0_5	0.0_0	2.2_0[g]		0.5_0[h]		0.0_0	0.0_0	0.0_0	0.6_0

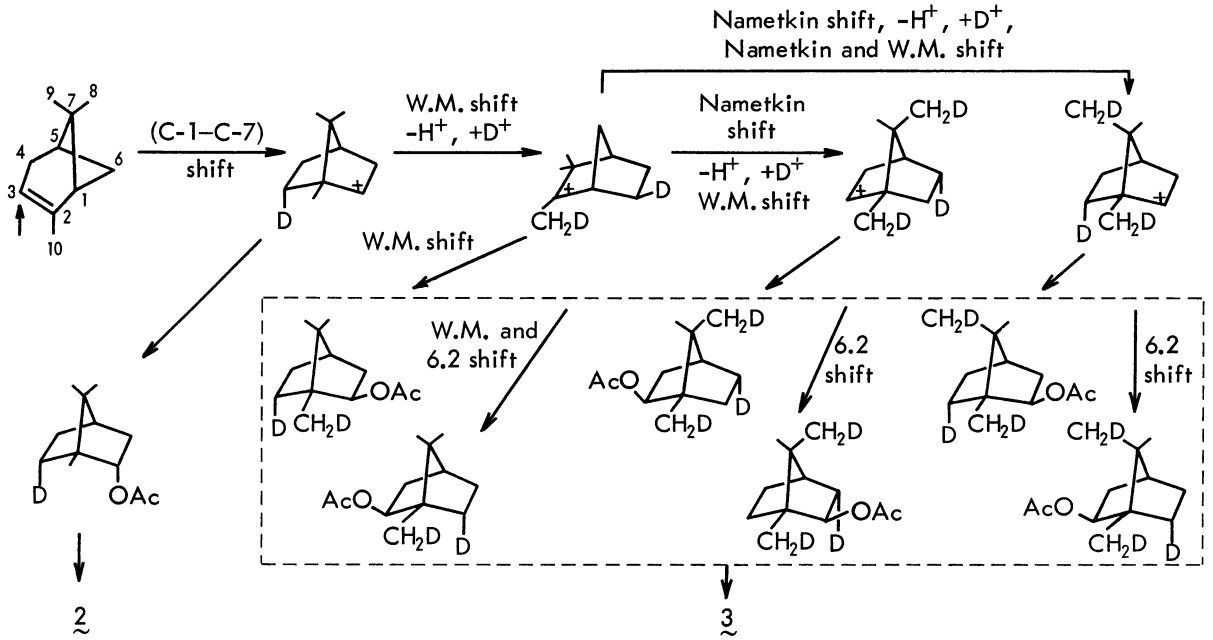
		2x	6n	8	10	6x	5n	7s	5x	4	7a	9
	S^c	+24.9	+15.8	+11.3	+8.0	+7.5	+7.5	+6.6	+5.5	+5.1	+5.0	+4.6
4	d	0.0_0	0.0_5	0.0_0	0.0_0	0.7_0	0.0_0	0.0_0	0.0_0	0.0_0	0.0_0	0.0_0
	e	0.0_0	0.2_0	0.0_0	0.1_0	0.9_0	0.0_0	0.0_0	0.0_0	0.0_0	0.0_0	0.0_5

		2n	3x	7s	10	3n	7a	6n	4	6x	8	9
	S^c	+24.2	+19.1	+13.7	+10.6	+9.4	+7.2	+6.8	+5.7	+4.7	+3.1	+3.0
5	d	0.6_5	0.0_0	0.4_0	1.3_0	0.0_0	0.4_5	0.0_0	0.0_0	0.0_0	0.4_5[i]	
	e,f											

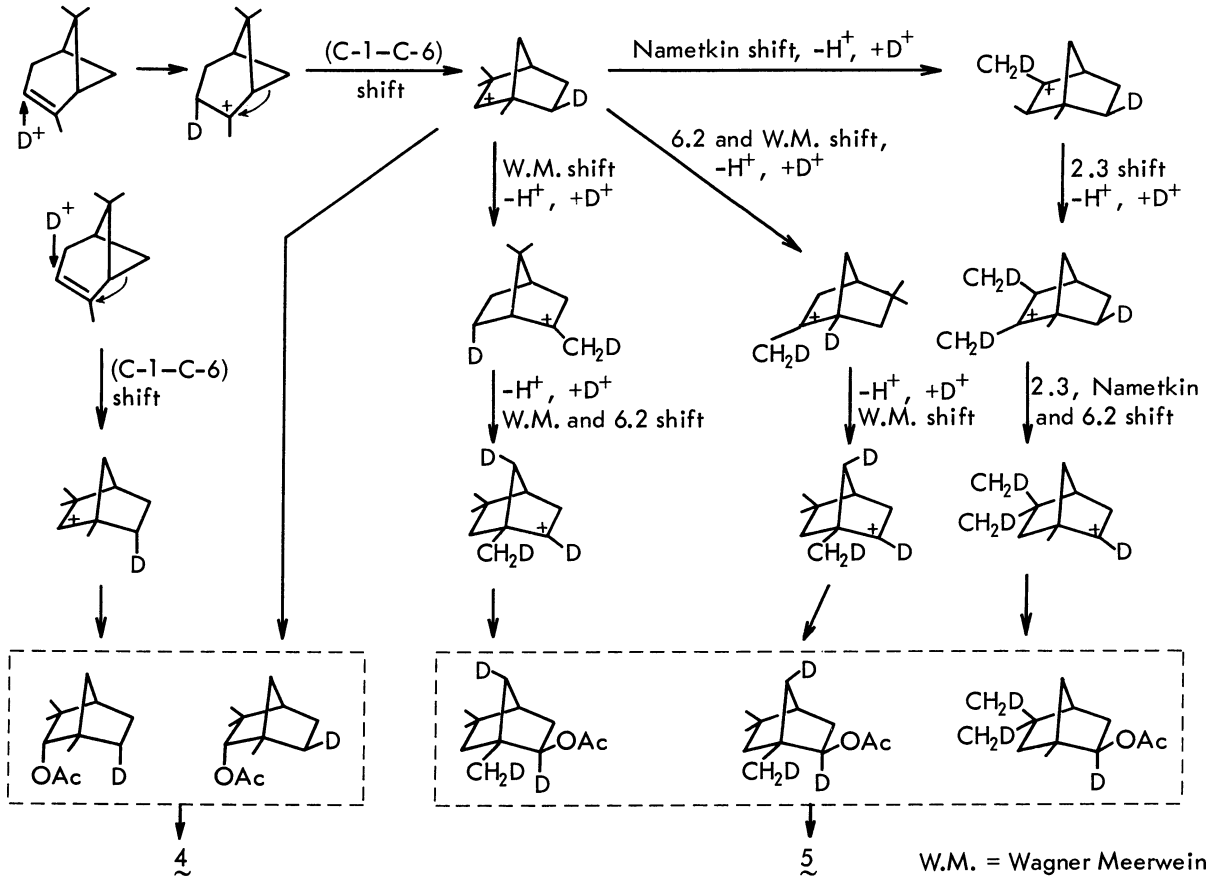
[a] Determined by integrated signal-intensity measurements of $Eu(DPM)_3$-assisted ^1H NMR spectra recorded on a Varian A-56/60D and/or an HA-100 spectrometer using $CDCl_3$ solutions containing internal TMS and various amounts of the complex. The rearrangement was carried out several times; only one typical example is shown here. [b] Abbreviations x, n, s, and a denote exo, endo, syn, and anti, respectively. [c] Slopes of initial linear parts of the $Eu(DPM)_3$-induced shift curves of proton signals determined for the undeuterated products. [d] Carried out under the condition (i) (see text). [e] Carried out under the condition(ii) (see text). [f] This product was not obtained under this reaction condition. [g] Solely incorporated in 10-Me. [h] Not found in position 4. [i] Almost equally distributed.

precision (ca. 5%) of D-content determinations by the signal integration method, we picked up the carbon sites incorporating more than 10% D-contents in order to discuss the pathways of D-incorporation (see Table I).[9]

The most significant feature in Table I is the fact that 2 obtained under both conditions has high D-contents at C-6 endo, and to considerable extents, at 10-Me,[10] whereas 3 has D-atoms scrambled into the sites of 10-, 9-, and 8-Me, and C-6, C-5, and C-3 endo, particularly under the more acidic condition involving B_2O_3. The D-scrambling difference between the endo- and the exo-alcohol was also observed between 4 (endo) and 5 (exo). This result can reasonably be explained by the difference in the D-incorporation steps shown in Schemes 1 and 2, where D-incorporation takes place in the first AcOD-addition step to 1 in the pathways to endo-derivatives, while in those to exo-derivatives, there are a lot of addition steps to unsaturated intermediates formed through Wagner-Meerwein-, Nametkin-, and C-6–C-2-shifts. The fact that the sum of the D-content in the



SCHEME 1. Pathways to Deuterium Incorporated Borneol (2) and Isoborneol (3).



SCHEME 2. Pathways to Deuterium Incorporated α-Fenchol (4) and β-Isofenchol (5).

six-membered ring carbons (C-1 ~ C-6) is less than unity is undertaken from the dilution of D^+ in the medium with H^+ liberated in the steps to the olefin formation.

The second significant feature is the fact that 4 obtained under the condition (ii)[11] has a considerable amount of D (20%) at the C-6 endo- as well as the C-6 exo-site (90%). This indicates that in the AcOD-addition step to 1, D^+ approaches to the double bond from both exo- (minor) and endo-sides (major) competitively.

The failure of the 7,7-dimethyl substituent of 1 in blocking the D^+-approach from the exo-side can be understood by assuming that C-1—C-6 participation became invovled in the step of the D^+-addition from the exo-side, giving an effective reduction of the steric hindrance of 7,7-dimethyls. The predominant formation of 2 enriched with D at C-6 endo can also be understood by both factors: C-1—C-7 participation involved in the step of the D^+-addition from the endo-side and the absence of the steric hindrance by 7,7-dimethyls.

The high preference of electrophiles on the exo-side even in the presence of 7,7-dimethyls in bicyclo[2.2.1]heptenyl systems[1] may also be interpreted in terms of the predominant effect of C-1—C-6 participation over the steric hindrance of a syn-methyl substituent at C-7. More precise determination of D-contents in the individual carbon sites in products 2-5 is now in progress using other methods.

References and notes

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9. Control experiments showed that acetic acid esters of 2, 3, and 4 did not indicate measurable interconversions among them under both reaction conditions and α-terpinyl acetate did not rearrange into isobornyl acetate under the condition (ii).
10. This is attributable to the D-incorporation in the step of the rearrangement of α-pinene ⇌ β-pinene, which is not shown in the Schemes to avoid confusion.
11. The absence of D-incorporation at the C-6 endo-site in the first treatment is tentatively attributable to the large steric requirement of the electrophile.

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