Regional NMR Facility (NIH No. RR542) at the University of Pennsylvania, where the 220-MHz NMR spectra were obtained.

Registry No.—**1**, 51446-90-3; **2**, 17974-52-6; **3**, 51446-91-4; **4**, 28890-28-0; **9**, 62861-88-5; *cis*-**10**, 62861-89-6; *trans*-**10**, 62861-90-9; **11**, 472-66-2; **12a**, 472-68-4; **12c**, 62861-91-0; **12d**, 62861-92-1; **13a**, 62861-93-2; **13b**, 51417-31-3; **13c**, 62861-94-3; **13d**, 62861-95-4; **14b**, 62861-96-5; **14d**, 62861-97-6.

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A Conformational Analysis of Cyclopropanodecalin Derivatives by Carbon-13 Nuclear Magnetic Resonance Spectroscopy[1]

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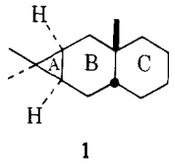
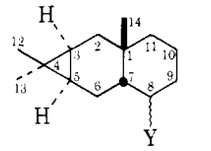
The ^{13}C NMR spectra of 18 cyclopropanodecalins based on the carane skeleton and containing a *cis*-decalin configuration have been recorded and all carbon shifts assigned. The β-deuterium isotope effect of some multiply deuterated compounds aided the shift assignment. On the basis of the shift data the hydrocarbons, alcohols, and acetates could be classified in terms of the two possible *cis*-decalin conformations.

The stereochemical and conformational features of a series of tricyclic substances derived from (−)-*cis*-caran-3-one have been the subject of recent chemical[3] and spectroscopic[3,4] studies, circular dichroism,[3] ^1H NMR,[3] IR,[3] and, in one instance, x-ray crystallographic, data[4] having been gathered on trimethylcyclopropanodecalin derivatives (**1**). The present communication represents an extension of the earlier ^{13}C NMR investigation of bicyclic carane derivatives[5] and reports the chemical shift assignment and conformational assessment of tricycles based on structure **1**.

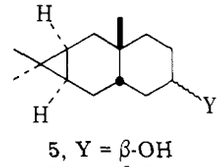


1

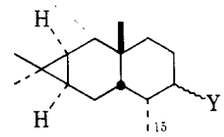
The compounds chosen for study consisted of the hydrocarbon **1**, nine derivatives possessing a single methyl, hydroxy, or acetoxy substituent on ring C (**2–6** and **15–18**) and eight derivatives containing two of these functions on ring C (**7–14**). For four of these substances, **1**, **5**, **15**, , and **16**, the assignment of seven of the decalin ring carbons has been obtained by a minimum number of deuteration experiments, making extensive use of the deuterium β-effect.[5,6] This technique has permitted the characterization of the conformationally impure members of this class of compounds.



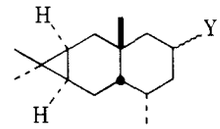
1, Y = H
2, Y = α-Me
3, Y = α-OH
4, Y = α-OAc
17, Y = β-OH
18, Y = β-OAc



5, Y = β-OH
6, Y = β-OAc
15, Y = α-OH
16, Y = α-OAc



7, Y = β-OH
8, Y = β-OAc
11, Y = α-OH
12, Y = α-OAc



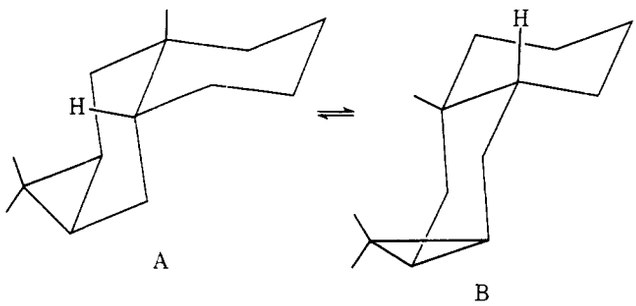
9, Y = α-OH
10, Y = α-OAc
13, Y = β-OH
14, Y = β-OAc

The B/C cis ring junction of these substances allows the skeleton to adopt conformation A or B or exist as a mixture of the two forms.[7] On the basis of conformational analysis, A is expected to be of lower energy in view of its avoidance of the severe nonbonded interaction of C(12) and C(14) in B. Furthermore, in the monofunctional derivatives possessing either

Table I. Chemical Shifts of Tricycles 1–10[a,c]

	1	2	3	4	5	6	7	8	9	10
C(1)	30.7	31.8	32.6	32.7	30.1	30.0	31.6	31.4	33.0	33.0
C(2)	34.9	35.2	34.7	34.6	33.7	33.6	34.1	34.1	34.9	34.8
C(3)	17.5	17.0	16.9	16.9	17.1	17.6	16.6	16.6	16.7	16.7
C(4)	16.7	16.6	16.7	16.7	16.7	16.6	16.7	16.5	16.6	16.7
C(5)	18.9	18.4	17.7	17.7	18.4	18.2	18.2	18.0	18.2	18.1
C(6)	20.4[b]	14.9	14.1	15.1	21.5	21.2	16.6	16.5	14.9	14.9
C(7)	36.2	41.6	42.4	39.8	36.8	36.6	42.7	42.5	40.5	40.5
C(8)	26.7	29.7	69.5	73.1	36.4	32.3	37.5	34.4	29.2	29.0
C(9)	19.6	27.4	28.2	24.7	66.4	69.8	71.4	74.3	37.5	33.0
C(10)	21.6[b]	21.7	20.2	20.0	31.1	27.0	31.1	27.3	67.7	71.1
C(11)	31.3	30.2	29.7	29.7	30.2	29.8	30.1	29.5	40.0	35.9
C(12)	15.5	15.5	15.4	15.5	15.3	15.2	15.3	15.2	15.5	15.2
C(13)	28.7	28.6	28.4	28.5	28.5	28.4	28.5	28.4	28.4	28.5
C(14)	27.0	26.8	26.6	26.5	26.9	26.7	26.9	26.7	27.5	27.3
C(15)		19.1					14.8	14.7	18.2	18.1
C=O				170.2		170.2		170.5		170.4
Ac Me				21.3		21.2		21.1		21.4

[a] In ppm downfield from Me_4Si; $\delta(Me_4Si) = \delta(CDCl_3) + 76.9$ ppm. [b] Assignments may be reversed. [c] Registry no.: 1, 62961-16-4; 2, 62961-17-5; 3, 62961-18-6; 4, 62961-19-7; 5, 62961-20-0; 6, 62961-21-1; 7, 62961-22-2; 8, 62961-23-3; 9, 62961-24-4; 10, 62961-25-5.



a *cis*-H(7)–H(8) or a *trans*-H(7)–H(9) configuration, the substituent adopts an equatorial stance in A, hence yielding to this conformer even greater preference over form B. This prediction has been borne out for the *p*-bromobenzoate of alcohol **5** in the solid state.[4] On the assumption of substances having only equatorial substituents in conformer A showing similar conformational behavior, these tricycles were submitted to ^{13}C NMR analysis first.

Chemical Shift Assignments

The dimethylcyclopropyl moiety is recognized readily from the equivalence of the carbon resonances of this group with those previously characterized among carane derivatives.[5] Thus, the *endo*- and *exo*-methyl signals appear at 15.4 ± 0.1 and 28.5 ± 0.1 ppm, respectively, and the resonance of their common quaternary carbon neighbor at 16.8 ± 0.2 ppm. The high-field cyclopropyl methines, C(3) and C(5), resonate over two narrow ranges, 17.1 ± 0.5 and 18.3 ± 0.6 ppm. Within each substance the low-field signal is allocated to C(5) on the basis of deuteration experiments (vide infra). While the methine values apply strictly only to substances with equatorial ring C substituents, deviations from these ranges exceed not more than a few tenths of a part per million in any of the derivatives.

After recognition of the *gem*-dimethylcyclopropyl signals, the angular methyl group and the bridgehead quaternary center in the 8α and 9β derivatives **2–4** and **5–6**, respectively, are unique carbon types identified by the multiplicity patterns of their single-frequency off-resonance decoupled (SFORD) spectra. The angular methyl group of **2** displays a sharp quartet pattern similar to that of each of the *gem*-methyl groups, whereas the components of the C(8) methyl quartet show greater half-widths due to residual two-bond carbon–hydrogen and/or second-order coupling.[8,9] The hydroxymethine and bridgehead methine signals in **3–6** are assigned routinely. The differentiation of the latter from C(8) in **2** follows from the practically equivalent β-effects of the hydroxy and methyl groups (cf. **2** and **3**). These considerations leave only the methylene signals of **2–6** to be assigned.

Comparison of the spectra of the alcohols **3** and **5** with their respective acetates identifies the centers attached to the carbinol carbon, i.e., C(9) of **3** and C(8) and C(10) of **5**, but does not differentiate the latter pair. Between **3** and **5** C(6) experiences the loss of a peri interaction and C(10) gains a β-effect. Hence these two carbons are expected to resonate at lower field in **5**, while two additional methylene peaks, C(2) and C(11), remain unaffected in the two alcohols and their acetates. These interrelationships specify the assignments given in Table I for C(6), C(9), and C(10) of the 8α-substituted compounds and C(6), C(8), and C(10) of the 9β-functionalized substances. Since alcohol **3** differs trivially from **2** at only the functionalized ring carbon, tentative assignments, except for the differentiation of C(2) from C(11), are complete for **2–6**.

The above shift allocations are corroborated by consideration of the *trans*-H(8)–H(9) and *cis*-H(8)–H(10) disubstituted derivatives **7** and **9** and their acetates. With reference to **2**, the introduction of an equatorial hydroxy group into **7** and **9** causes the perturbation of two ring carbons aside from the newly substituted site. The methylene carbons β to the hydroxy group in **9** are shifted downfield 10 ppm from their position in **2**. The C(11) shift identifies, by difference, the ca. 35 ppm resonance as the only methylene signal remaining constant in **2–10** and, hence, as the signal of C(2).

Apart from the resonances of the C(6)–C(9) fragment of **1**, the spectrum of this hydrocarbon bears a strong resemblance to that of **2**. However, three methylene signals within 2 ppm of each other leave the assignments based solely on chemical shift correlations uncertain. The resonances of four of the six methylene centers in this substance have been proven by deuteration experiments (vide infra). Carbon(10) is assigned tentatively the 21.6-ppm signal, a value identical with the C(10) resonance of **2**. All carbons shifts of compounds **1–10** are listed in Table I.

The conformation of the above substances is implicit in the chemical shift relationships between the mono- and disubstituted derivatives. Thus, for example, on comparison of **9** and **2**, the hydroxy group causes insignificant perturbations at all sites other than C(9), C(10), and C(11), the substituted and β carbons. The conspicuous absence of γ-effects relegates the oxygen function to an equatorial orientation. This fact and

Table II. Chemical Shifts of Tricycles 11–18[a,e]

	11	12	13	14	15	16	17	18
C(1)	31.6	31.4	31.3	31.3	29.2	29.4	31.0	30.7
C(2)	35.1	35.0	35.4	35.1	28.0	29.4	31.4[b]	32.4
C(3)	17.1	16.8	17.1	17.0	19.0	18.6	18.5	17.9
C(4)	16.7	16.7	16.9	17.0	17.9	17.7	17.4	17.2
C(5)	18.4	18.3	18.6	18.4	18.8	18.7	18.4	17.9
C(6)	16.7	16.5	14.6	14.6	22.1	21.8	18.5[c]	19.0[d]
C(7)	40.9	40.6	41.2	40.8	38.2	37.3	45.7	41.4
C(8)	33.7	32.8	24.7	25.5	37.4	33.0	71.4	74.1
C(9)	70.9	72.9	34.4	31.4	69.6	71.7	30.9[b]	26.4
C(10)	29.9	26.9	68.1	71.2	31.3	27.3	18.7[c]	18.1[d]
C(11)	25.3	25.8	37.5	34.0	37.4	34.8	36.3	34.1
C(12)	15.4	15.4	15.4	15.4	15.5	15.4	15.3	15.3
C(13)	28.5	28.4	28.5	28.4	29.0	28.8	28.6	28.4
C(14)	26.7	26.6	30.0	29.1	30.0	29.2	30.3	29.3
C(15)	15.1	14.8	18.6	18.4				
C=O		170.2		170.2		170.0		170.1
Ac Me		21.3		21.6		21.3		21.4

[a] In ppm downfield from Me_4Si; $\delta(Me_4Si) = \delta(CDCl_3) + 76.9$ ppm. [b,c,d] Assignments may be reversed. [e] Registry no.: **11**, 62961-26-6; **12**, 62961-27-7; **13**, 62961-28-8; **14**, 62961-29-9; **15**, 62961-07-3; **16**, 62961-08-4; **17**, 62961-09-5; **18**, 62961-10-8.

the known relative configuration of these substances[3] are sufficient to define their conformation as A. The possibility of some members of the series **1–10** being conformer mixtures, with significant proportions of B present, is excluded by the constant C(2) resonance which, as shown below, is highly sensitive to conformational change. Examination of Table I reveals the C(2) resonance appears over the narrow range of 35.0 ± 0.4 ppm, exclusive of compounds **5–8**. The latter four substances, whose C(2) signal is ca. 1 ppm upfield, have a common equatorial C(9) oxy substituent. This perturbation is likely the result of polarization of the C(1)–C(2) bond by the carbon–oxygen dipole, which should show its strongest effect on the C(1)–C(2) axis when emanating from an equatorial C–O bond [cf. the C(2) shifts in the hydroxy epimers of **5** and **7** in Table II]. Additional examples of long-range, ϵ shieldings attributable to hydroxy substitution in equivalent molecular arrays, i.e., *trans*-4-alkylcyclohexanols contained within conformationally rigid skeleta, indicate the regularity of the effect and require an explanation that does not invoke atomic interaction or conformational mobility.[10]

Four disubstituted derivatives of **1**, i.e., **11–14**, possess one axial and one equatorial substituent on ring C. Hence, irrespective of the conformational disposition of these substances, the axial group interacts 1,3-diaxially with a single alkyl substituent, either the angular methyl group or C(6). While 1,3-diaxial alkyl–alkyl and alkyl–hydroxyl interactions need not be energetically equivalent, the overriding factor determining the conformer preference remains, to a first approximation, the C(1)–C(4) methyl–methyl interaction. On this basis it may be anticipated that compounds **11–14** are further representatives of conformer A, in which the oxygen function assumes an axial orientation. Spectral comparison of **11** and **13** with their epimeric hydroxy counterparts, **7** and **9**, respectively, confirms this assessment. In particular, the conformational weathervane C(2) (vide supra) is equivalent, except as noted above, for both of these substances and their acetates. The axial hydroxy group of **11** is revealed by mild shielding of C(8), C(9), and C(10) and the strong γ-effect (5 ppm) suffered by C(11) relative to **7**. A cogent argument establishing the axial orientation of the hydroxy group is the insignificant shift of C(8) accompanying acetylation. In three of the four possible stereoisomers of unsymmetrical, chair-like, vicinally hydroxylated and methylated cyclohexanes acetylation results in 2.5–4.0 ppm shielding of the centers bound to the carbinol carbon. These shieldings are examples of γ-effects in which the oxygen substituent interacts sterically with the hydrogen at the oxycarbon sites. This interaction is not possible with the hydrogen of the methine holding the methyl group in the cis isomer in which the oxygen function is axial. Analogous behavior is observed in cases of O-methylation.[11,12]

The C(8) methyl resonance of **13** and **14** is the same as that of **9** and **10**, while the angular methyl group is shifted ca. 2.5 ppm downfield from its location in the latter substances. The magnitude of this δ-effect is typical of the response of methyl functions opposed by a *syn*-diaxial hydroxy group.[13] This effect and the normal magnitude of γ-effects of the same group in **11** and **13** [cf. C(11) of **11** and **7** and C(8) of **9** and **13**] suggests the absence of any unusual deformation of ring C in these substances. The foregoing considerations establish that all substances **1–14** have a common, unique conformation in which the angular methyl group is axial with respect to ring C, as in A. All chemical shifts of compounds **11–14** are listed in Table II.

An unambiguous assessment of the ground-state energy difference of the alternate conformers of **15–18** is impossible. These substances contain a single ring C substituent stereochemically oriented in such a way as to introduce a destabilizing *syn*-diaxial oxygen–alkyl interaction into the otherwise preferred conformer A. In fact, the spectra of these substances do not correlate with **1–14** except for the conformationally insensitive *gem*-dimethylcyclopropyl moiety. Furthermore, the curious behavior of both **15** and **17** accompanying acetylation indicates these compounds to be represented not by a unique conformation, but rather to be conformer mixtures. Comparison of **15** and **16**, for instance, shows four of the five methylene signals to undergo 2–4-ppm shifts, a result which defies simple explanation unless a change in the equilibrium concentration of alternate conformers exists between **15** and its acetate.

This circumstance negates the usual criteria employed in signal assignment and requires an alternate method of chemical shift evaluation. The technique chosen for this purpose entails inspection of deuterated analogues of the protio compounds under carefully controlled conditions to allow recognition of the small deuterium β-effects (2–3 Hz per deuterium in the absence of proximate heteroatoms) as well as the directly deuterated carbons.

The pentadeuterio hydrocarbon **25** and alcohols **22** and **23** were prepared by known literature procedures (Scheme I). The starting material (−)-*cis*-caran-3-one was converted into its trideuterio derivative **19** with loss of stereochemical integrity at C(4) by carbonate-induced exchange in deuterium oxide–dioxane solution. After Robinson annelation and two

Table III. Chemical Shift and Shift Differences Between Protio and Deuterio Tricycles[a]

	1	25[f]	Δδ[b]	5	22[f]	Δδ	15	23	Δδ	16[c]	24[c,f]	Δδ
C(1)	30.70	30.67	–	30.09	30.02	−2	29.15	*d*		29.36	*d*	
C(2)	34.91	34.89	–	33.72	33.70	–	28.03	28.10	+2	29.36	29.44	+2
C(3)	17.50	17.50	–	17.11	17.11	–	18.95	18.93	–	18.56	18.51	–
C(4)	16.67	*d*		16.65	*d*		17.91	17.84	–	17.69	17.64	–
C(5)	18.88	18.69	−5	18.41	18.25	−4	18.78	18.64	−4	18.66	18.51	−4
C(6)	20.35	*e*		21.49	*e*		22.05	*e*		21.81	*e*	
C(7)	36.19	35.93	−7	36.84	36.60	−6	38.20	37.96	−6	37.28	36.99	−7
C(8)	26.70	26.46		36.41	*e*		37.39	*e*		33.04	*e*	
C(9)	19.63	19.34	−7	66.39	66.39	0	69.64	69.42	−6	71.72	71.67	−1
C(10)	21.61	*e*		31.13	*e*		31.32	*e*		27.28	*e*	
C(11)	31.28	31.14	−4	30.16	29.92	−6	37.35	37.11	−6	34.81	34.55	−7
C(12)	15.49	15.49	–	15.27	15.27	–	15.49	15.49	–	15.37	15.39	–
C(13)	28.71	28.72	–	28.46	28.47	–	28.98	28.96	–	28.81	28.83	–
C(14)	27.00	26.95	–	26.91	26.92	–	30.02	30.02	–	29.22	29.19	–

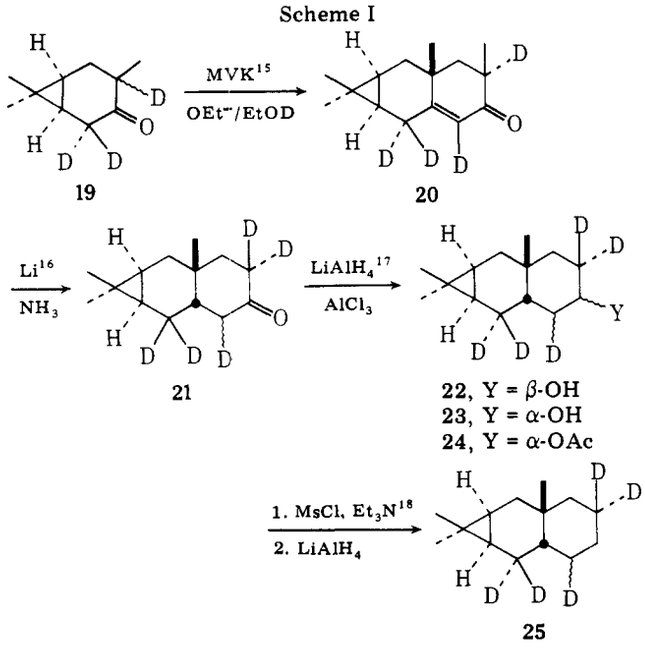
[a] Chemical shifts in ppm downfield from Me_4Si; $\delta(Me_4Si) = \delta(CDCl_3) + 76.9$ ppm. [b] $\Delta\delta = \delta$(deuterio derivative) − δ(protio derivative), expressed in Hz. Digital resolution = ±0.6 Hz. Negative sign indicates an upfield shift. [c] Acetate carbonyl and methyl signals reported in Table II. [d] Signal not detected. [e] Deuterated carbon signal not detected. [f] Registry no.: **22**, 62930-39-6; **24**, 62930-40-9; **25**, 62930-41-0.

reductions alcohol **22** was reduced further to hydrocarbon **25** and alcohol **23** was acetylated, thus yielding 6,6,8,10,10-pentadeuterio analogues of **1**, **5**, **15**, and **16**.[14]

The spectrum of **25** contains two less signals than that of **1**. The slowed rate of dipolar relaxation of fully deuterated carbons, splitting of the resonance by one-bond C–^{2}H coupling, and broadening of all resonances of carbons two and three bonds from the deuterium atom contribute to the vanishingly low intensity of the C(6) and C(10) signals. The monodeuterated site, C(8), is detected as a low-intensity, broad 1:1:1 triplet centered at 26.5 ppm in the proton noise-decoupled spectrum (see Table III). In the remaining deuterated compounds, however, the monodeuterated methylene signal was not observed due to small amounts of available material and, hence, low spectral signal-to-noise ratios.

The pattern of deuterium incorporation in **25** is arranged in such a manner as to yield to each member of undeuterated methylene and methine sets a different number of β-deuterons. Thus the methylenes C(2), C(11), and C(9) and the methines C(3), C(5), and C(7) possess zero, two, and three β-deuterium neighbors, respectively. On the assumption of the small, upfield deuterium β-effects being approximately additive and γ-effects being negligible, the resonances of these six carbons can be assigned unambiguously by the magnitude of their shifts in **25** vs. those of **1**. The correlation of these spectra is presented in Table III. The assumption of insignificant γ and longer range effects is supported fully by the invariant resonances of C(2), C(3), and the methyl groups (<1 Hz change). Carbon-2 is unique, being the only methylene to remain constant in **1** and **25**. Among the two cyclopropyl methines of **25** C(3) has no deuterium neighbors and is constant, whereas C(5) experiences a 5-Hz upfield shift. This shift is due to two β-deuterons and implies that each deuterium shows a 2–3-Hz β-effect. The three β-deuterons of the unambiguous C(7) methine of **25** yield a 7-Hz perturbation of this carbon's resonance, corroborating the approximate magnitude and additivity of the β-deuterium effects. Hence, the upfield 7 and 4 Hz shifts of the 19.6- and 31.3-pp methylene resonances of **1** in its deuterated analogue relegate these signals to C(9) and C(11), respectively, and complete the assignment of this hydrocarbon.

Scheme I

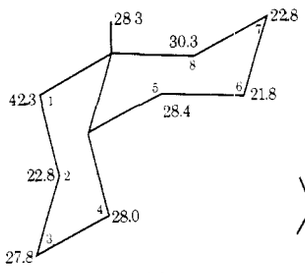


The shift changes between alcohols **5** and **22** parallel closely those of the hydrocarbons, except at the oxygenated site which does not reflect the presence of β-deuterons. Despite attempts to maintain identical conditions, the anomalous shift of the oxycarbon may reflect different degrees of hydrogen bonding, causing perturbations as large as the deuterium β-effects. The assignments dictated by the deuterium results (Table III) are in full accord with those given in Table I.

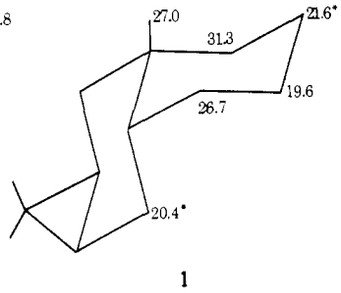
A similar correlation of **15** and **16** with their pentadeuterio derivatives **23** and **24**, respectively, yields a complete assignment of the undeuterated ring carbons of these substances independent of chemical shift relationships (see Table III). Among the directly deuterated carbon resonances of **15** the high-field 22-ppm resonance is not altered by acetylation (cf. **15** and **16**) and therefore is allocated to C(6) (vide infra). The C(8) and C(10) signals of **15** are differentiated by comparison with **5** and are discussed below with respect to the conformational stance of the compound.

In comparison to derivatives **1**–**14** the C(2) resonance of alcohol **15** has undergone a dramatic upfield shift. A large shift change at this position has analogy in the chemical shifts of *cis*-9-methyldecalin (**26**).[19] A strong likeness of the angular methyl and ring C carbon resonances of hydrocarbon **1** to equivalent centers in **26** is apparent on the formulas below. The flattening of ring B of **1** by the cyclopropyl function must alter the γ-effects of ring B carbons acting on ring C centers and hence exact correspondence of these resonances with those of like carbons of **26** cannot be expected. However, two sets of shifts suggest that **26** is a realistic model for the tricyclic

substances. The conformational mobility of **26** at room temperature averages the neopentyl centers C(1) and C(8) as well as C(3) and C(6). These two resonance pairs are the only conformationally diagnostic signals, since the remaining, averaging carbon pairs, C(2)–C(7) and C(4)–C(5), have nearly equal δ values in both conformers due to similar environments and accidental degeneracy, respectively. The large 12-ppm difference of the neopentyl methylenes of **26** and the approximate correspondence of ring C shifts between **26** and **1** indicate qualitatively that the C(2) and C(11) resonances of **1** exhibit probably large, inversely proportional shift perturbations between conformers A and B. While **1** exists exclusively as A, **15** does not. In fact, the C(2) and C(11) shifts of the latter display shift modifications in consonance with those predicted from model **26**. Compared with **5**, C(2) of **15** is shifted upfield 5.7 ppm and C(11) downfield 7.1 ppm. The larger shift change at C(11) must take into account also the partial loss of the γ-effect from the hydroxy group in conformer B. The fortuitous cancellation of shift perturbations which yield similar C(4) and C(5) δ values in **26** is reflected also in the conformationally insensitive C(6) resonance between **5** and **15** (vide supra).



26



1

The proportions of the A and B contributions to the description of **15** cannot be calculated accurately, since the δ values the C(2) and C(11) resonances would possess in conformer B are not known. However, an approximate assessment is possible. The chemical shift of C(10) in **5** and **15** is nearly identical. To the extent the behavior analogous to that of *cis*-9-methyldecalin (**26**) is observed at this site, i.e., equal γ-effects at C(10) from the angular methyl group in conformer A and from C(2) in conformer B, the C(10) resonance implies that **15** is represented exclusively by conformer B. Though this center is not expected to be changed significantly by the skeletal reorientation between A and B, the C(9) hydroxy group exerts a β-effect, equivalent to that in **5**, only in an equatorial disposition. The oxymethine resonance of **15** is 3.2-ppm downfield of the same signal of **5**. In the latter substance, which adopts conformation A, the hydroxy group is equatorial and the carbinol carbon suffers a γ-effect from C(6). The oxymethine of **15**, depicted as conformer B, is environmentally equivalent to that in **5** except for the removal of the C(6) γ-effect. Whereas this difference is low for a normal γ-effect (cf. C(3) and C(6) of **26**), independent support for the weakness of the γ-effect between C(6) and C(9) is found in a comparison of **7** and **11**. The γ-effect suffered at C(6) from C(9) in **7** is replaced with a δ-effect from the hydroxy group in **11**, but the normally expected 2–3-ppm downfield δ-effect is not observed. This suggests that the terminal carbons of the C(6)–C(9) fragment may be splayed slightly from the interannular gauche geometry found in the *cis*-decalin **26**. The attenuated δ-effect strongly implies a weakened γ-effect. These qualitative correlations indicate that alcohol **15** is preponderantly conformer B.

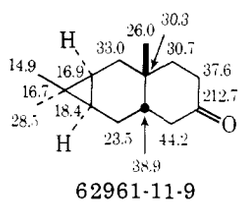
Accompanying the normal upfield shifts of C(8) and C(10) of **15** upon acetylation (**15** → **16**), C(2) shifts downfield 1.4 ppm and C(11) upfield 2.6 ppm. The latter shifts are tending toward the δ values these carbons exhibit in **5** and hence signal a shift in the equilibrium conformer proportions between **15** and its acetate **16**, increasing the contribution of form A. Since the A values of the hydroxy and acetoxy functions in hydrogen donor solvents are similar,[20] differing by <500 cal, the shift in conformational equilibrium between **15** and **16** indicates a very small ground-state energy difference between conformers A and B for these derivatives and assigns a somewhat smaller A value to the acetoxy function.

Alcohol **17**, if depicted as conformer A, possesses a single axial ring C hydroxy group involved in a 1,3-diaxial interaction with the angular methyl group, hence being energetically similar to **15**. Whereas a deuterated derivative of this substance was not prepared and thus the assignment of the methylene resonances not proved by independent means, the unusual shift modification of these signals occurring on acetylation (**17** → **18**) are analogous to those observed between **15** and **16** and indicate the substances to be conformer mixtures. The C(2) resonance of **17** lies closer to the 35-ppm value this signal assumes in A-like conformers than the same signal in **15** or **16**, indicating the further diminution of the contribution of B for **17**.

The C(6) signal can be used also to judge the conformational preference of **17**. As discussed above, in the absence of C(8) substituents the C(6) signal is insensitive to the conformational make-up of the compound and appears at 21–22 ppm. The γ-effect at C(6) from the C(8) hydroxy group of **17** should be strong in conformer B in which these centers adopt a vicinal trans-diequatorial stance and absent in A wherein they become trans-diaxial. With 5 ppm as the magnitude of the γ-effect (cf. C(6) of **1** and **7**)[21] and 21.5 ppm as the δ value of C(6) the 18.7 (or 18.5) ppm resonance of C(6) in **17** suggests A and B contribute equally to the conformational description of this substance.

In the acetate of **17**, i.e. **18**, the C(2) resonance moves downfield (to 32.4 or 34.1 ppm). This shift direction is analogous to that in the **15** → **16** change and points to an increasing contribution from form A. Simultaneously C(11) moves downfield (to 32.4 or 34.1 ppm). These requirements are fulfilled irrespective of the shift designation of C(2) and C(11) of **18**. The assignments given in Table II are preferred, since the reverse allocation, i.e., 34.1 ppm to C(2), would imply that the acetate is represented almost exclusively as conformer A, a conclusion incompatible with the intermediate C(6) resonance.

As a sidelight to the above study, the carbon shifts of the ketone precursors of the alcohols used in the investigation were determined. The δ values are depicted on the ketone formulas.



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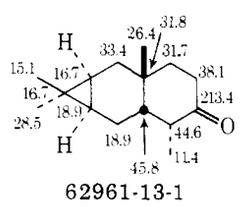

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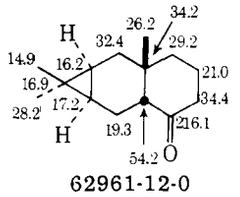

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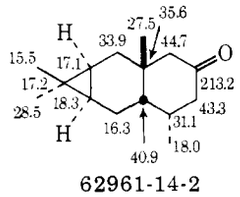

62961-14-2

Experimental Section

The carbon shifts in the tables and the last four formulas were recorded with $CDCl_3$ solutions on a Varian XL-100-15 spectrometer operating at 25.20 MHz in the Fourier transform mode.

Registry No.—**26**, 2547-26-4.

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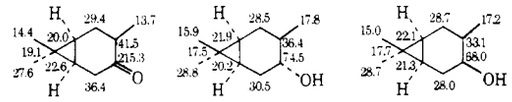
(14) Compound **19** (4β-Me) and the two epimeric alcohols derived therefrom by hydride reduction also were examined spectrally. The deuterium shifts necessitate the assignment reversal of the C(4) and *endo*-methyl resonances of the ketone and allow the previously undifferentiated cyclopropyl methines in all three substances to be assigned, as shown on the following formulas.



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(21) The γ-effect may also be assessed as the methyl shift difference between methylcyclohexane and *trans*-2-methylcyclohexanol, i.e., 4.7 ppm.[22]
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Organic Reactions at Alumina Surfaces. A Mechanistic and Synthetic Study of Sulfonate Ester Elimination Reactions Effected by Chromatographic Alumina[1,2]

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Chromatographic, neutral, highly active Woelm alumina has been used at room temperature for high-yield dehydrosulfonation of some secondary cyclic and acyclic and some primary sulfonate esters. Evidence is presented for the concertedness of these olefin-forming elimination reactions, and application is made to gram-scale chemospecific elimination of sulfonic acids from some highly functionalized esters. The scope and limitations of this heterogeneous procedure are presented, and the practical advantages and disadvantages are noted. Some practical guidelines are suggested for which activity of alumina is needed for optimal elimination reactions, and some generalizations are made concerning the structural types of sulfonate esters which would be most suitable for this alumina promoted dehydrosulfonation reaction.

The very large number of olefin-forming elimination reactions indicates the importance of alkenes as synthetic intermediates and as ultimate target molecules.[3] Because of this importance, new reagents and new synthetic methods are constantly being sought which offer some advantages over known procedures for alkene formation.[4] Recently we have developed a very mild, convenient, and high-yield method for converting some sulfonate esters into the corresponding olefins even in the presence of normally base and acid labile (e.g., carboxylic ester) groups; even some neopentylic tosylates undergo elimination *without skeletal rearrangement*, and in all cases product isolation is easy. These concerted, heterogeneous elimination reactions are effected simply by stirring solutions of the sulfonate esters over untreated[5a] or vacuum-dehydrated[5b] commercial Woelm chromatographic alumina at room temperature. This procedure has some practical advantages over other methods for overall dehydration of alcohols, and it has been chosen recently by other laboratories to prepare some cycloalkenes.[6] We now conclude our study of this alumina procedure by illustrating its application to preparative scale (several grams) reactions, by demonstrating its chemoselectivity in converting a steroidal tetraester into the corresponding olefinic triester, and by extending its scope to conversion of primary cyclohexylmethyl tosylate esters into methylenecyclohexanes. The mechanistic and synthetic aspects of the discussion are organized according to the type of organic reactant: (1) secondary cyclic systems; (2) secondary acyclic systems; and (3) primary systems.

Results and Discussion

Secondary Cyclic Systems. Sulfonate esters are known to undergo concurrent elimination and hydrolysis reactions when exposed to chromatographic alumina.[7,8] We have studied the effect of alumina activity (i.e., dryness) on the ratio of dehydrosulfonation to hydrolysis using Woelm neutral activity I,[5a] activity super-I (W-200-N), and activity super-I-dehydrated (W-200-N-Dehydrated)[5b] alumina.[9] Of these three types of alumina, W-200-N-Dehydrated alumina converts sulfonates into the corresponding olefins with the least amount of alcohol (i.e., hydrolysis) side products; however, W-200-N-Dehydrated alumina has the operational disadvantages of having to be prepared by 400 °C vacuum dehydration of commercially available W-200-N alumina and having to be used immediately after preparation. For convenience and operational simplicity, we have therefore recently examined commercially available W-200-N alumina itself; we now report that *untreated W-200-N alumina used directly from the commercial can* is sufficiently dry to convert substituted *cyclohexyl* tosylates into the corresponding olefins with very little (<2%) or, in some cases, with no alcohol side