Stereochemistry and Regiochemistry of Electron Impact Thermally and Photolytically Induced Eliminations from 2-Decalyl Acetates

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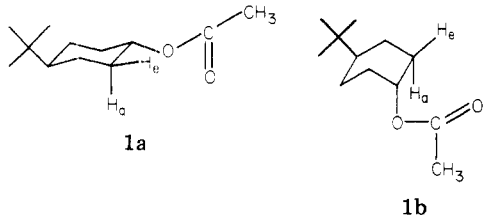
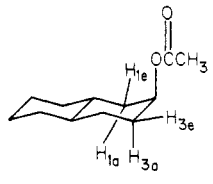
Deuterium-labeled compounds are used to define the stereochemistry and regiochemistry of the electron impact induced elimination of acetic acid from *trans,trans*-2-decalyl acetate and *trans,cis*-2-decalyl acetate. Both compounds fragment with very predominant abstraction of equatorial hydrogen atoms. Since the trans equatorial hydrogens of the trans,trans acetate cannot be approached within the requisite 1.8 Å by the acetate carbonyl in any boatlike conformer, this result demonstrates that hydrogen abstraction largely occurs from the chair conformer of the cyclohexyl ring. Both compounds fragment with predominant elimination toward C-1 rather than C-3. The regiochemistry of the pyrolysis of the acetates and the photolysis of the corresponding phenylacetates is compared with that of the mass spectral elimination.

The internuclear distances and angles of the chair conformer of the cyclohexyl ring system are well defined. This fact has been exploited to probe the stereochemistries and mechanisms of numerous reactions. Mass spectroscopists have generally been unable to attempt analogous studies on electron impact induced fragmentations because many of these reactions apparently occur through high energy conformationally ill-defined boatlike conformers. For example, the predominant mechanism of the electron impact induced dehydration of cyclohexanols involves such conformers.[1] Similarly, the elimination of acetic acid from 1-tetralyl acetate involves hydrogen abstraction from C-4 via a boatlike conformer.[2] In contrast, and perhaps more encouragingly, several lines of evidence have recently led to the conclusion that *cis*- and *trans*-4-alkylcyclohexyl acetates and related derivatives undergo γ-hydrogen abstraction while largely in the stable chair conformation.[3-6] A major argument in support of this hypothesis is provided by the observation that elimination of acetic acid from *trans*-4-*tert*-butylcyclohexyl acetate (1) involves predominant loss of the trans equatorial hydrogen.[3] Solution chemistry experiments have demonstrated that trans equatorial hydrogen abstraction will predominate if reaction in fact occurs from the chair conformer.[4] Conversely, the cis axial hydrogen is much more readily approached by the acetate carbonyl in most boatlike conformers (e.g., **1b**). The force of this argument is weakened by the existence of a minority of boatlike conformers in which the carbonyl oxygen can approach the trans equatorial hydrogen within the requisite[7] 1.8 Å for hydrogen abstraction. Thus, if these conformers were particularly reactive, or particularly abundant, they could be the source of the observed stereochemistry. In order to remove this ambiguity, and thus to provide a model system of well-defined geometry for future studies, a more constrained cyclohexyl ring system has been selected for this investigation. Drieding models demonstrate that in the *trans,cis*-2-decalyl acetate **3** (2β,4aα,8aβ-decahydro-2-naphthalenol acetate) the C-1 and C-3 trans equatorial hydrogens are accessible to the carbonyl oxygen in the stable chair conformer. Conversely, in all boatlike conformers, these hydrogens are well beyond the requisite 1.8 Å for abstraction, while the cis axial hydrogens are readily approached more closely. Thus, determining the stereochemistry of hydrogen abstraction from C-1 and C-3 may permit a clear-cut demonstration of the conformation of the cyclohexyl ring.



1a

1b



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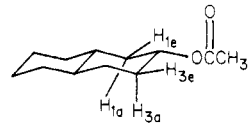

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A second reason for undertaking these experiments is to define the regiochemistry of hydrogen abstraction. A priori, γ-hydrogen abstraction might occur either from C-1 or C-3. Elucidation of the extent of hydrogen abstraction from these positions may permit conclusions about the mechanism of the process, especially if the decalyl ring system is demonstrated to be a chairlike conformer. Apparently, no attention has yet been devoted to revealing the fairly subtle factors which must control the site of γ-hydrogen abstraction in systems in which the competing hydrogens should have similar migratory aptitudes (e.g., all are secondary and unactivated).

Results

The mass spectra of *trans,cis*-2-decalyl acetate **3** and *trans,trans*-2-decalyl acetate **2** (2α,4aα,8aβ-decahydro-2-naphthalenol acetate) exhibit intense peaks at m/e 136, corresponding to the elimination of acetic acid from the molecular ion (for **3**, the m/e 136 and 137 peaks comprise 28% of the total ion current above m/e 40 at 70 eV, 90% at threshold, while for **2**, the corresponding figures are 25 and 80%). No second-field free-region metastables were detected for the genesis of these peaks. Extremely weak first-field free-region metastables were detected for formation of m/e 136 from the molecular ion of **2** and **3**; in each case a more intense metastable was observed for loss

(1) For a recent review, see: Green, M. M. *Top. Stereochem. 1976*, **9**, 35.
(2) Wojinski, S.; Gross, M. L. *Org. Mass. Spectrom. 1979*, **14**, 135.
(3) Eadon, G.; Gold, P.; Bacon, E. *J. Am. Chem. Soc. 1975*, **97**, 5184.
(4) Eadon, G. *J. Am. Chem. Soc. 1976*, **98**, 7313. Eadon, G.; Jefson, M. *J. Org. Chem. 1976*, **41**, 3917.
(5) Eadon, G., *Org. Mass. Spectrom. 1977*, **12**, 674.
(6) Rej, R. N.; Bacon, E.; Eadon, G. *J. Am. Chem. Soc. 1979*, **101**, 1668.
(7) Beard, C.; Wilson, J. N.; Budzikiewicz, H.; Djerassi, C. *J. Am. Chem. Soc. 1964*, **86**, 269. Djerassi, C.; von Mutzenberger, G.; Fajks, J.; Williams, D. H.; Budzikiewicz, H. *Ibid. 1965*, **87**, 817. Williams, D. H.; Wilson, J. N.; Budzikiewicz, H.; Djerassi, C. *Ibid. 1963*, **85**, 2091.

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Table I. Electron Impact Induced Loss of Acetic Acid from *trans,trans*-2-Decalyl Acetate and Labeled Analogues[a]

compd	isotopic purity[b]	$(M^{+\cdot} - OAc)$[c]	$(M^{+\cdot} - HOAc)$[c]	$(M^{+\cdot} - H_2OAc)$ or $(M^{+\cdot} - DOAc)$[c]	(DOAc loss[d,e]/ HOAc loss)
trans,trans-2-decalyl acetate (2)		12	100	3	
trans,trans-2-decalyl-*1,1,3,3-d*$_4$ acetate (2-d_4)	96% d_4	4	26	100	
trans,trans-2-decalyl-*1α-d* acetate (2-*1α-d*)	99% d_1	12	100	7	0.05 ± 0.03
trans,trans-2-decalyl-*1β-d* acetate (2-*1β-d*)	97% d_1	12	98	100	1.35 ± 0.02
trans,trans-2-decalyl-*3α-d* acetate (2-*3α-d*)	99% d_1	12	100	7	0.05 ± 0.03
trans,trans-2-decalyl-*3β-d* acetate (2-*3β-d*)	97% d_1	12	100	29	0.28 ± 0.02

[a] Data were recorded at 70 eV, using a heated inlet system (200 °C) and a source temperature of 70–110 °C. Peak intensities represent the average of four determinations and are reproducible to ± 1 intensity unit. [b] Determined from the mass spectrum of the appropriate trimethylsilyl ether. [c] Raw data, averaged over four distinct sets of measurements. [d] Ratio corrected for isotopic impurities (d_0 and ^{13}C), extraneous fragmentations ($M^{+\cdot} - OAc$ and $M^{+\cdot} - H_2OAc$), and hydrogen abstraction from sites other than C-1 and C-3. Error limits include extreme values observed in four distinct sets of measurements. [e] These ratios have been calculated for ionizing voltages between 70 eV and threshold; within experimental error, the ratios agree at all ionizing voltages. However, at ionizing voltages near threshold, error limits are considerably increased.

Table II. Electron Impact Induced Loss of Acetic Acid from *trans,cis*-2-Decalyl Acetate and Labeled Analogues[a]

compd	isotopic purity[b]	$(M^{+\cdot} - OAc)$[c]	$(M^{+\cdot} - HOAc)$[c]	$(M^{+\cdot} - H_2OAc)$ or $(M^{+\cdot} - DOAc)$[c]	(DOAc loss[d,e]/ HOAc loss)
trans,cis-2-decalyl acetate (3)		12	100	3	
trans,cis-2-decalyl-*1,1,3,3-d*$_4$ acetate (3-d_4)	96% d_4	2	23	100	
trans,cis-3-decalyl-*1α-d* acetate (3-*1α-d*)	97% d_1	12	100	11	0.08 ± 0.02
trans,cis-2-decalyl-*1β-d* acetate (3-*1β-d*)	95% d_1	12	99	100	1.25 ± 0.03
trans,cis-2-decalyl-*3α-d* acetate (3-*3α-d*)	97% d_1	12	100	8	0.05 ± 0.02
trans,cis-2-decalyl-*3β-d* acetate (3-*3β-d*)	96% d_1	12	100	30	0.26 ± 0.02

[a] Data were recorded at 70 eV, using a heated inlet system (200 °C) and a source temperature of 70–110 °C. Peak intensities represent the average of four determinations and are reproducible to ± 1 intensity unit. [b] Determined from the mass spectrum of the appropriate trimethylsilyl ether. [c] Raw data, averaged over four distinct sets of measurements. [d] Ratio corrected for isotopic impurities (d_0 and ^{13}C), extraneous fragmentations ($M^{+\cdot} - OAc$ and $M^{+\cdot} - H_2OAc$), and hydrogen abstraction from sites other than C-1 and C-3. Error limits include extreme values observed in four distinct sets of measurements. [e] These ratios have been calculated for ionizing voltages between 70 eV and threshold; within experimental error, the ratios agree at all ionizing voltages. However, at ionizing voltages near threshold, error limits are considerably increased.

Table III. Relative Rates of Hydrogen Abstraction in the Electron Impact Induced Elimination of Acetic Acid from 2-Decalyl Acetates

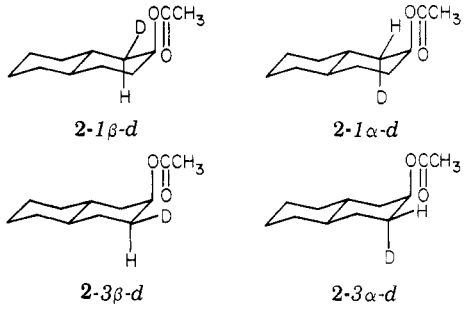
compd	hydrogen atom	rel rate of elimination
trans,trans-2-decalyl acetate (2)	C-1β	1[a]
	C-1α	0.1 ± 0.04
	C-3β	0.4 ± 0.05
	C-3α	0.1 ± 0.04
trans,cis-2-decalyl acetate (3)	C-1β	1[a]
	C-1α	0.15 ± 0.04
	C-3β	0.4 ± 0.05
	C-3α	0.09 ± 0.04

[a] Arbitrarily defined.

of protonated acetic acid (61 amu) from the molecular ion. Thus, studies of the stereochemistry and regiochemistry of acetic acid loss among metastable ions were precluded.

The mass spectra of the *1,1,3,3-d*$_4$ analogues of **2** and **3** demonstrate that acetic acid loss involves predominantly abstraction of a C-1 or C-3 hydrogen (Table I and II). Correcting the raw data for isotopic impurities (^{13}C and d_3) and extraneous processes (OAc and H_2OAc loss) demonstrates that 90% of acetic acid loss from **3**-d_4 involves deuterium elimination; the corresponding figure for the axial acetate **2**-d_4 is 88%.

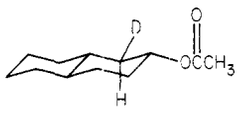
A series of stereospecifically monodeuterated *trans,trans*-2-decalyl acetates (**2**-*1β-d*, **2**-*1α-d*, **2**-*3β-d*, and **2**-*3α-d*)



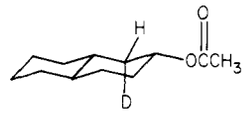
2-*1β-d* **2**-*1α-d*

2-*3β-d* **2**-*3α-d*

and *trans,cis*-2-decalyl acetates (**3**-*1β-d*, **3**-*1α-d*, **3**-*3β-d*, and **3**-*3α-d*) were prepared to establish the stereochemistry of the hydrogen abstraction step. The results obtained when these compounds were subjected to electron impact induced fragmentation appear in Tables I and II. The last column in Tables I and II contains the result of a calculation of the ratio of deuterium loss to protium loss from C-1 and C-3 for each monodeuterated isomer. These ratios have been corrected for extraneous fragmentation pro-



3-1β-d



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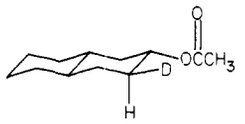
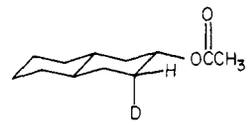


3-3β-d



3-3α-d

cesses (OAc and H_2OAc loss), isotopic impurities (^{13}C and d_0), and hydrogen loss from positions other than C-1 and C-3. The last correction was derived from consideration of the spectra of **2**-d_4 and **3**-d_4 and assumes an isotope effect $k_H/k_D = 1.2$. Although this value was initially derived from earlier studies,[3,6] subsequent calculations (vide infra) confirm that it is appropriate for these compounds.

The ratios appearing in the last column of Tables I and II were calculated from data obtained with an ionizing voltage of 70 eV. However, no significant trend could be detected in these ratios as the ionizing voltage was lowered to the threshold for accurate measurement. The values calculated from data obtained at the threshold for accurate measurement (nominally 12 eV) agreed with those tabulated, within experimental error.

The entries in the last columns of Tables I and II can be used to calculate the "relative rates" of elimination of each hydrogen on C-1 and C-3. Thus, for example, it can be written that

$$\left(\frac{M^{+\cdot} - DOAc}{M^{+\cdot} - HOAc}\right)_{2\text{-}1\beta\text{-}d} = \frac{k_{1\beta}/I}{k_{1a} + k_{3\beta} + k_{3\alpha}}$$

where the quantity in parentheses is the ratio of DOAc loss to HOAc loss from C-1 and C-3 for compound **2**-1β-*d*, I is the isotope effect (k_H/k_D), $k_{1\beta}$ and $k_{3\beta}$ are respectively the average rate constants for abstraction of a β (equatorial) hydrogen from C-1 and C-3, and $k_{1\alpha}$ and $k_{3\alpha}$ are the corresponding rate constants for abstracting the appropriate α(axial) hydrogen. Three analogous equations can be written relating I and the four average rate constants $k_{1\beta}$, $k_{3\beta}$, $k_{1\alpha}$, and $k_{3\alpha}$ to the ratios [(M$^{+\cdot}$ - DOAC)/(M$^{+\cdot}$ - HOAc)] for the remaining three monodeuterated isomers of the *trans,trans*-2-decalyl acetate **2**. Elimination of the four rate constants from this system of equations generates a sixth order expression in I; its solution corresponds to $I = 1.23 \pm 0.15$. These equations can also be solved for the relative rate ratios. The results of this calculation appear in Table III.

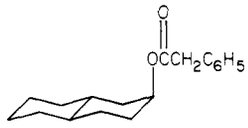
In a similar manner, four equations can be written relating the data obtained for the *trans,cis*-2-decalyl acetate **3** to I and the average rate constants for abstraction of each C-1 or C-3 hydrogen. Solution of these equations for I generates a value of 1.25 ± 0.15. Table III contains the results of the calculation of the relative rates of abstraction of each hydrogen.

In an effort to gain insight into the origins of the relative rate ratios appearing in Table III, formally analogous reactions were sought for comparison. The regiochemistry of the pyrolysis of **2** and **3** has already been reported.[8] The photolysis of phenylacetates has been demonstrated to result in the elimination of phenylacetic acid with stepwise hydrogen abstraction through a cyclic six-membered transition state.[9,10] Thus, the phenylacetates **4** and **5** were prepared and photolyzed (254 nm, hexane solvent). The results of this study of the regiochemistry of the photoelimination appear in Table IV.

Table IV. Comparison of the Regiochemistry of Pyrolytic, Photolytic, and Electron Impact Induced Eliminations of 2-Decalyl Esters

compd	reagent	C-1 abstraction/C-3 abstraction
trans,trans-2-decalyl acetate (2)	Δ	1.3[a]
trans,trans-2-decalyl phenylacetate	hγ	0.66 ± 0.05
trans,trans-2-decalyl acetate (2)	EI	2.1
trans,cis-2-decalyl acetate (3)	Δ	0.75[a]
trans,cis-2-decalyl phenylacetate	hγ	0.40 ± 0.03
trans,cis-2-decalyl acetate (3)	EI	2.4

[a] Data taken from ref 8.



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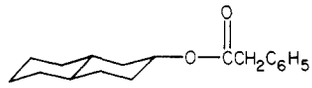

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Discussion

The stereochemistry of electron impact induced hydrogen abstraction in the fragmentation of the *trans,trans*-2-decalyl acetate **2** and the trans,cis isomer **3** generally parallels that observed for the corresponding 4-*tert*-butylcyclohexyl acetate. The axial acetate **2** exhibits very predominant loss of the cis equatorial hydrogens from C-1 ($k_{1\beta}/k_{1\alpha} = 10$) and C-3 ($k_{3\beta}/k_{3\alpha} = 4$). This result is consistent with (but does not require) hydrogen abstraction predominantly from the chair conformer of the cyclohexyl ring; the carbonyl oxygen cannot approach the trans axial hydrogen closely in this conformation. Further, the stereospecific behavior observed here provides strong evidence for the integrity of the acetate-bearing cyclohexyl ring. Much less stereospecific abstraction would be observed if free rotation about the C-1–C-2 or C-2–C-3 bonds were possible.[11]

More interesting is the observation that the *trans,cis*-2-decalyl acetate **3** also exhibits very predominant abstraction of the C-1 ($k_{1\beta}/k_{1\alpha} = 6.7$) and C-3 ($k_{1\beta}/k_{1\alpha} = 4.4$) equatorial hydrogens. These high stereospecificities corraborate the conclusion that the cyclohexyl ring is intact prior to hydrogen abstraction. Further, they require that hydrogen abstraction occurs predominantly from the stable chair conformer. Models demonstrate that in every relaxed boatlike conformer the equatorial hydrogen is well beyond the requisite[7] 1.8 Å O–H internuclear distance for abstraction, while the axial hydrogen is invariably capable of being approached more closely. In the stable chair conformer, the acetate carbonyl can approach the equatorial or axial hydrogens equally closely (ca. 1.2 Å). The preferential abstraction of the equatorial hydrogen in this conformer has been observed in solution-chemistry studies[4,10] and has been attributed to unfavorable steric interactions in the transition state for axial hydrogen abstraction.[3,4,10]

(8) Huckel, W.; Rucker, D. *Justus Liebigs Ann. Chem. 1963*, **666**, 30.
(9) Yarchak, M. L.; Dalton, J. C.; Saunders, W. H. *J. Am. Chem. Soc. 1973*, **95**, 5224. *Ibid. 1973*, **95**, 5228.
(10) Eadon, G.; Bacon, E.; Gold, P. *J. Org. Chem. 1976*, **41**, 171.
(11) Green, M. M.; Moldowan, J. M.; McGrew, J. G. *J. Org. Chem., 1974*, **39**, 2166.

These experiments also permit determination of the regiochemistry of the hydrogen abstraction step. Both 2-decalyl acetates exhibit preferential loss of the C-1 (rather than C-3) hydrogen atoms, $(k_{1\alpha} + k_{1\beta})(k_{3\alpha} + k_{3\beta}) = 2.2$ for the axial acetate **2** and 2.3 for the equatorial acetate **3**. Consideration of molecular models suggests no clear reason why the C-1 hydrogens should be especially mobile; the steric interactions involved in abstracting a C-1 or a C-3 equatorial hydrogen appear very similar.

In order to test this hypothesis, the regiochemistries of several formally analogous eliminations were sought for comparison. The pyrolysis of acetates **2** and **3** results in the elimination of acetic acid through a cyclic six-membered transition state with concerted hydrogen migration and C–O bond cleavage;[12] no significant preference for formation of the Δ^1 alkene was observed (Table IV).[8] The photolysis of the corresponding phenylacetates **4** and **5** results in elimination of phenylacetic acid with stepwise migration of hydrogen through a cyclic six-membered transition state.[9] Here too, no marked preferences were observed for C-1 hydrogen abstraction (Table IV). Thus, unless the transition state geometry for electron impact induced γ-hydrogen abstraction is markedly different from that of both formally similar processes, the explanation for the observed regiochemistry is not steric.

Other explanations for preferential C-1 hydrogen abstraction can be excluded by the data obtained here. Abstraction of a C-1 or a C-3 hydrogen formally generates isomeric ionized alkenes; however, the observed effect cannot be due to preferential second-generation fragmentation of the ionized Δ^2 alkene. At threshold, 80–90% of the total ion current in the spectra of **2** and **3** corresponds to the $M^{+\cdot}$ – HOAc process. Even if the entire population of daughter ions arose from the Δ^2-alkene ion, this effect would be too small to account for the observed regiochemistry. Similar reasoning can be used to exclude the preferential fragmentation of the intermediate C-3 radical to other ionic products.

Nevertheless, a number of explanations could conceivably account for the observed regiochemistry. For brevity's sake, only one will be tentatively advanced here. The disfavored carbon (C-3) is attached to C-4 (a secondary carbon) while C-1 is attached to a tertiary carbon (C-8a). Thus, if the transition state for hydrogen abstraction results in a deficiency of electron density at the carbon bearing the migrating hydrogen, the electron releasing inductive effect of the tertiary carbon at C-8a would facilitate C-1 hydrogen abstraction more effectively than the secondary C-4 carbon would facilitate C-3 hydrogen abstraction. Unfortunately, little attention has been devoted to the details of the transition state for hydrogen migration,[13] or even to the nature of the migrating species (hydride, hydrogen atom, or proton).[14] However, even if it is assumed that hydrogen atom transfer occurs (the most conventional assumption), some positive charge may develop at the γ-carbon in the transition state for γ-hydrogen abstraction. There is considerable evidence for such charge separation in intermolecular hydrogen abstraction reactions induced by chlorine radicals ("polar effects").[15] Since the ionized carbonyl must be very electrophilic, even greater charge separation might result in the mass spectral case. Nevertheless, this explanation is a tentative one. Further experimentation will be required to prove or disprove it.

Conclusions

trans,trans-2-Decalyl acetate **2** loses acetic acid with predominant abstraction of cis equatorial hydrogens. This result requires that the cyclohexyl ring remains intact at least until hydrogen abstraction occurs and is fully consistent with reaction from the stable chair conformer. *trans,cis*-2-Decalyl acetate **3** fragments with predominant loss of trans equatorial hydrogen atoms. This result is only consistent with predominant hydrogen abstraction from the stable chair conformer. Unambiguous demonstration of the conformation of these reacting ions, combined with earlier results,[3-6,10] places existing studies on the mechanisms and stereochemistries of electron impact induced hydrogen abstraction on a firmer footing[6] and makes additional studies possible.

Both acetates **2** and **3** exhibit marked preferences for abstraction of C-1 rather than C-3 hydrogen. Studies of the regiochemistry of two formally analogous reactions (pyrolysis of acetates and photolysis of the corresponding phenylacetates) suggest that the origin of this effect is not steric. A tentative hypothesis is advanced to account for this effect.

Experimental Section

Mass spectra were obtained on an AEI MS902 mass spectrometer, using a heated all-glass inlet system; source temperatures were maintained at 70–110 °C during these measurements. All acetates were purified by preparative gas chromatography (10 ft × 0.125 in. column packed with 10% UCW 98 on 80/100 Chromosorb S) prior to mass spectral analysis. They were prepared from the corresponding alcohol, using the pyridine–acetic anhydride procedure.[3-6] Other gas chromatography employed a 10 ft × 0.125 in. 10% Apiezon L on 60/80 acid washed DMCS column or a 20 ft × 0.25 in. 20% diglycerol on 80/100 Chromosorb P column. NMR spectra were obtained using deuteriochloroform solvent on a Varian Model A-60 spectrometer. Unless otherwise indicated, column chromatography was performed on Activity II Alumina, using benzene as eluent.

trans,cis-1-Decalol (1β,4aα,8aβ-decahydronaphthalenol) was prepared by reduction of *trans*-1-decalone[16] with lithium tri-*sec*-butylborohydride.[16,17] A solution of 5.02 g (33 mmol) of the ketone in 25 mL of THF was added to 1.2 equiv (40 mL of a 1 M solution) of the reducing agent cooled to −78 °C in a N_2 atmosphere. After 3 h, the mixture was allowed to warm to room temperature. Oxidation (alkaline hydrogen peroxide) followed by extractive workup generated crude *trans,cis*-1-decalol (4.8 g, 94%). Column chromatography gave 3.9 g of pure alcohol, mp 54–55 °C (lit.[18] mp 55 °C). The alcohol was demonstrated to be at least 98% pure, based on its gas chromatographic behavior (diglycerol column at 150 °C). NMR, IR, and mass spectra were consistent with the proposed structure.

***trans*-Δ¹-Octalin (1,2,3,4,4a,5,6,8a-octahydronaphthalene)** was prepared by pyrolysis (450 °C) of the acetate of *trans,cis*-1-decalol.[8] Gas chromatography[19] (Apiezon L at 120 °C) demonstrated that *trans*-Δ¹-octalin was the principal (>95%) product. The alkene was separated from tarry and polar impurities by column chromatography (silica gel, pentane eluent) and distillation (Kugelrohr). NMR and IR spectra were in accord with the proposed structure.

***trans,cis*-2-Decalol-1α-*d* (2β,4aα,8aβ-decahydronaphthalenol-1α-*d*) and *trans,trans*-2-decalol-1β-*d* (2α,4aα,8aβ-decahydronaphthalenol-1-*d*)** were prepared by

(12) Saunders, W. H., Jr.; Cockerill, F. "Mechanisms of Elimination Reactions"; Wiley: New York, 1973; Chapter 8.
(13) Boer, F. P.; Shannon, T. W.; McLafferty, F. W., *J. Am. Chem. Soc. 1968*, **90**, 7239.
(14) Spiteller, G.; Spiteller-Friedmann, M. *Monatsh. Chem. 1964*, **95**, 257. McLafferty, F. W.; Wachs, T. *J. Am. Chem. Soc. 1967*, **89**, 5043. Budzikiewicz, H.; Djerassi, C.; Williams, D. H. "Mass Spectrometry of Organic Compounds"; Holden-Day: San Francisco, 1967; Chapter 3.
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deuterioboration of *trans*-Δ^1-octalin.[3,20] Gas chromatography (diglycerol column at 150 °C) demonstrated that the four possible alcohols were formed in comparable yields; purification was therefore accomplished by preparative gas chromatography. The most rapidly eluted alcohol (16%, retention time 54 min) exhibited mp (54 °C), NMR and IR, and VPC retention time identical with those of authentic *trans,cis*-1-decalol. The second component (30%, retention time 76 min) was identified as *trans,cis*-2-decalol-*1α-d* (**2**-*1α-d*). It exhibited mp 52–53 °C (lit.[8] mp 53 °C), NMR and IR, and VPC retention time identical with those of the authentic unlabeled molecule (isolated from a commercial sample).[16] Since the alcohol did not exhibit a $M^{+\cdot}$ in its mass spectrum, the trimethylsilyl ether was prepared. It exhibited $M^{+\cdot}$ at *m/e* 227 ($C_{13}H_{25}DOSi$).

The third eluted alcohol (30%, retention time 60 min) exhibited physical and spectral characteristics[8,19] consistent with the expected *trans,trans*-1-decalol-*2β-d* structure. Finally, *trans,trans*-2-decalol-*1β-d* (24%, retention time 92 min) was obtained. It exhibited mp 75–76 °C (lit.[20] mp 75 °C), NMR and IR, and VPC retention time identical with those of the authentic unlabeled compound. The trimethylsilyl ether exhiited $M^{+\cdot}$ at *m/e* 227 ($C_{13}H_{25}DOSi$).

trans,cis*-2-Decalol-*1β-d (**2β,4aα,8aβ-decahydronaphthalenol-*1β-d***) was prepared from pure deuterated *trans,trans*-2-decalol by an oxidation–reduction sequence.[3,6] Jones oxidation of 0.075 g of the axial alcohol at 0 °C for 1 h followed by a rapid extractive workup and subvacuo removal of solvent gave 0.110 g of crude *trans*-2-decalone-*1β-d*. The crude ketone was immediately reduced with $LiAlH_4$ to produce a mixture of 2-decalols in which the equatorial alcohol was heavily predominant. Column chromatography gave 0.038 g of the pure *trans,cis*-2-decalol-*1β-d* whose melting point and spectra were identical with those of an authentic unlabeled sample. The mass spectrum of the corresponding trimethylsilyl ether exhibited $M^{+\cdot}$ at *m/e* 227 ($C_{13}H_{25}DOSi$).

trans,trans*-2-Decalol-*1α-d (**2α,4aα,8aβ-decahydronaphthalenol-*1α-d***). Treatment of the epoxide mixture (generated from the reaction of *trans*-Δ^1-octalin with *m*-chloroperbenzoic acid) with $LiAlD_4/AlCl_3$ generated a mixture of *trans,trans*-2-decalol-*1α-d* and *trans,cis*-1-decalol-*2β-d*.[3,6,20,22] Preparative gas chromatography (diglycerol column at 150 °C) generated a pure sample of the title alcohol whose physical and spectral characteristics were identical with those of authentic unlabeled compound. The corresponding trimethylsilyl ether exhibited $M^{+\cdot}$ at *m/e* 227 ($C_{13}H_{25}DOSi$).

trans,cis*-2-Decalol-*3α-d and ***-3β-d*** (**2β,4aα,8aβ-decahydronaphthalenol-*3α-d*** and ***-3β-d***) and ***trans,trans*-2-decalol-*3α-d*** and ***-3α-d*** (**2α,4aα,8aβ-decahydronaphthalenol-*3α-d*** and ***-3b-d***) were prepared by procedures strictly analogous to those used for formation of the 1-labeled alcohols, using *trans*-Δ^2-octalin (1,2,3,4,4aα,5,8,8aβ-octahydronaphthalene) as the starting material. However, the greater symmetry of the Δ^2-octalin greatly simplified the isolation of pure alcohol products. Deuterioboration of *trans*-Δ^2-octalin gave only *trans,cis*-1-decalol-*3α-d* and *trans,trans*-1-decalol-*3β-d*. These alcohols were readily separated by column chromatography. Similarly, the $LiAlD_4/AlCl_3$ opening of *trans*-decalin 2,3-epoxide gave essentially only *trans,trans*-2-decalol-*3α-d*.

Photolysis of *trans,trans*-2-Decalyl Phenylacetate and *trans,cis*-2-Decalyl Phenylacetate. Photolyses were conducted according to the general procedures of Yarchak, Dalton, and Saunders.[9] The phenylacetates were irradiated as thoroughly degassed 0.01 M solutions in hexane, using an eight-lamp Rayonet preparatory reactor equipped with Rayonet RPR 2537 Å lamps. The isomer distribution of the resulting alkenes was determined by gas chromatography on an Apiezon L column at 120 °C. The alkenes exhibited retention times and mass spectra identical with those of authentic samples of *trans*-Δ^1-octalin and *trans*-Δ^2-octalin. The relative proportions of the two alkenes were unchanged (within experimental error) as the amount of starting material consumed was varied from 5–50%.

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Registry No. **2**, 66964-89-4; **2**-d_4, 71912-19-1; **2**-*1α-d*, 71912-20-4; **2**-*1β-d*, 71912-21-5; **2**-*3α-d*, 71912-22-6; **2**-*3β-d*, 71962-38-4; **3**, 66964-88-3; **3**-d_4, 71912-23-7; **3**-*1α-d*, 71912-24-8; **3**-*1β-d*, 71912-25-9; **3**-*3α-d*, 71962-39-5; **3**-*3β-d*, 71962-40-8; **4**, 71912-26-0; **5**, 71912-27-1; *trans*-1-decalone, 21370-71-8; *trans,cis*-1-decalol, 2529-03-5; *trans*-Δ^1-octalin, 2001-49-2; *trans,cis*-2-decalol-*1α-d*, 71912-28-2; *trans,trans*-2-decalol-*1α-d*, 71912-29-3; *trans,trans*-1-decalol-*2β-d*, 71912-30-6; *trans,cis*-2-decalol-*1β-d*, 71912-31-7; *trans*-2-decalone-*1β-d*, 71912-32-8; *trans,cis*-2-decalol-*1β-d* trimethylsilyl ether, 71912-33-9; *trans,trans*-2-decalol-*1α-d*, 71912-34-0; *trans,trans*-2-decalol-*1α-d* trimethylsilyl ether, 71912-35-1; *trans,cis*-2-decalol-*3α-d*, 49644-48-6; *trans,cis*-2-decalol-*3β-d*, 71962-41-9; *trans,trans*-2-decalol-*3α-d*, 49644-47-5; *trans,trans*-2-decalol-*3β-d*, 49644-27-1; *trans*-Δ^2-octalin, 2001-50-5.

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Effects of Protonation and Hydrogen Bonding on Nitrogen-15 Chemical Shifts of Compounds Containing the >C=N̈- Group[1a]

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The effects of solvent changes from chloroform to trifluoroethanol to trifluoroacetic acid on the chemical shifts of nitrogen-15 resonances have been determined for fourteen imines, four oximes, and two pyridines. Upfield shifts were observed for all of the compounds in trifluoroethanol and trifluoroacetic acid, ranging from 8 to 28 ppm in the first and from 110 to 150 ppm in the second. These shift changes can be attributed to hydrogen bonding and protonation, respectively. The hydrogen-bonding shifts can be generally rationalized through consideration of the basicities of the nitrogens involved while the protonation shifts seem mostly influenced by the degree of substitution by phenyl groups, as expected from changes in the substantial contributions to the >C=N̈- type nitrogen shifts from the second-order paramagnetic effect.

Over the last 15 years, effects of protonation on ^{14}N and ^{15}N resonances have been investigated for various types of nitrogen compounds.[2-10] Whereas these effects are usually relatively small in the case of aliphatic amines,

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