added. The suspension was stirred at room temperature for 1 hr, then at reflux for 7–8 hr. The mixture was cooled to room temperature, 4.0 ml of methyl iodide was added, and stirring was resumed at room temperature for 0.5 hr, then at reflux for 3 hr. The mixture was again cooled to room temperature and another portion of sodium amide (0.80 g) was added, and the sequence was repeated. Four cycles of this sequence were completed. The bulk of ether and of excess methyl iodide was removed by distillation through a 36-in. spinning-band column. Cold 3% sulfuric acid (30 ml) was added dropwise with external cooling to the residue. This mixture was extracted thoroughly with ether, and the combined ether extracts were washed with aqueous sodium thiosulfate and with brine, dried over anhydrous sodium sulfate, and the ether distilled through a spinning-band column until the volume of solution remaining was *ca.* 5 ml. Components of the ether solution (norcamphor-*d*, epimeric monomethylated norcamphors-*d*, and camphenilone-*d*) were separated by preparative gas chromatography. Camphenilone-4-*d* (0.122 g) was shown to be pure by analytical gas chromatography, and mass spectrometry indicated the composition: 89.5% 1-D and 10.5% O-D. Polydeuterated material was not detected.

Homoenolization. A *t*-butyl alcohol solution of camphenilone-4-*d* (0.193 *m* volume) and potassium *t*-butoxide (1.57 *m* volume) was sealed under nitrogen in a Pyrex tube and heated at 185° for 200 hr. The mass spectrum of camphenilone-4-*d* recovered from the reaction was essentially identical with that of the starting material (89.7% 1-D, 10.3% O-D). The recovered camphenilone-4-*d* was dissolved in *t*-butyl alcohol (ketone *ca.* 0.18 *m* volume) containing potassium *t*-butoxide (1.78 *m* volume), and the solution was heated at 185° for 300 hr. The mass spectrum of camphenilone recovered from this repeat reaction gave the species composition: 89.1% 1-D and 10.9% O-D.

The residue, after mass spectral analysis, was dissolved in ether and examined by sensitive analytical gas chromatography. The only volatile components observed (column temperature 145°) were solvent, camphenilone (retention time 10 min, 35 sec), and an unidentified impurity (*ca.* 1% of camphenilone concentration; retention time 8 min, 23 sec).

Camphenilone-7-*d*. Preparation. (+)-Camphor (10.2 g, mp 177.5–178°, α +43°) was deuterated by reflux for 9 hr in a solution of methanol-O-*d* and methanol (30 ml, *ca.* 70% O-D) made 1.4 *M* in sodium methoxide. Camphor-*d* (sublimed) from this first exchange was refluxed for 32 hr in a solution of methanol-O-*d* (15 g, 99% D) and deuterium oxide (7 g, 99.5% D) in which freshly cut sodium (1.1 g) had been dissolved. Recovered camphor-*d* (7.9 g, sublimed) was shown to be 94.2% dideuterated and 5.8% monodeuterated by mass spectrometry. This camphor-*d* and *p*-toluenesulfonylhydrazine (*ca.* 10% excess) were dissolved in dioxane (100 ml, previously treated with 1.0 ml of deuterium oxide and dried with anhydrous sodium sulfate) containing 1.0 ml of concentrated deuterium chloride in deuterium oxide (prepared by passage of deuterium chloride gas through deuterium oxide), and the solution was refluxed for 6 hr. The solution was poured into cold water (400 ml), and the white precipitate was washed with water, dried, and recrystallized from dry carbon tetrachloride, to yield 9.24 g (55%) of camphor-*d* *p*-toluenesulfonylhydrazone, mp 165–166° (lit.[4] mp 163–164°). This derivative was converted to camphenilone-7-*d* by the method reported earlier.[1] Preparative gas chromatography gave 0.054 g; analytical gas chromatography and mass spectrometry indicated the presence of camphor (*ca.* 4%).[20] The mass spectrum showed the isotopic distribution of camphenilone-7-*d* to be 25% 2-D, 49.5% 1-D, and 25.5% O-D.

Homoenolization. A *t*-butyl alcohol solution of this camphenilone-7-*d* (0.26 *m* volume) containing potassium *t*-butoxide (0.84 *m* volume) was heated at 185° for 98 hr. The mass spectrum of recovered ketone indicated 24.5% 2-D, 49.5% 1-D, and 26% O-D. The recovered ketone was redissolved in *t*-butyl alcohol containing potassium *t*-butoxide (2.26 *m* volume, ketone concentration 0.12) and heated at 185° for 200 hr. Camphenilone-*d* recovered from this reaction had a mass spectrum essentially identical with that taken earlier: 24.5% 2-D, 49.5% 1-D, and 26% O-D.

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(20) This trace of camphor was observed in earlier preparations (part IV, ref 27).

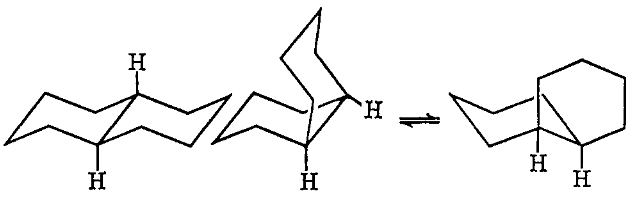
Nuclear Magnetic Resonance Spectroscopy. Conformational Equilibrations of *cis*-Decalins[1]

J. T. Gerig and John D. Roberts

Contribution No. 3337 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California. *Received January 26, 1966*

Abstract: The fluorine-19 magnetic resonance spectra of 2,2-difluoro-*cis*-decalin and some of its derivatives have been examined as a function of temperature. For several cases it was possible to determine the rates and activation energy for interconversion of the two possible chair–chair conformations of the compounds. In other instances, the point of equilibrium was found to be such that only one isomer predominated to the extent that kinetic studies were impossible. For 2,2-difluoro-*cis*-decalin, the activation energy was determined to be 14.0 ± 0.8 kcal/mole. The activation energy decreased to 9.7 ± 0.6 kcal/mole upon substitution of alkyl groups at the ring junctions. With methyl groups at the 1, 2, or 6 positions, one isomer was favored to the degree that equilibration could not be detected.

Inspection of models of the *cis* and *trans* forms of decalin which have the rings in the chair forms shows that there is only one *trans*-decalin (I) but that the *cis* isomer has two conformational isomers (IIa,b) which can be interconverted by flipping each ring in a manner similar to the familiar inversion of cyclohexane. The forms IIa and IIb are enantiomers and *cis*-decalin is expected to exist largely, if not completely, as a nonresolvable *d,l* pair of conformational isomers.



I IIa IIb

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(1) Supported in part by the National Science Foundation and the Office of Naval Research; presented at the 19th National Organic Symposium of the American Chemical Society, Tempe, Ariz., June 17, 1965.

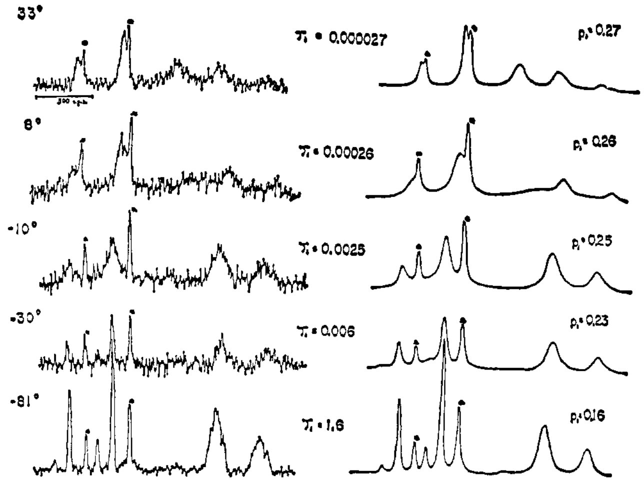


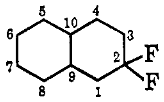
Figure 1. Experimental and calculated spectra of 2,2-difluoro-*cis*-decalin in acetone. The calculated spectra are composites made up of 29% of the spectrum of the *trans* isomer and 71% of the spectrum of the *cis* isomer. Only the spectrum of the *cis* isomer changes with temperature. Transitions marked with a star arise from the equatorial fluorine nucleus of the *trans* material. The left side of each spectrum starts at 0 cps, relative to trifluoroacetic acid.

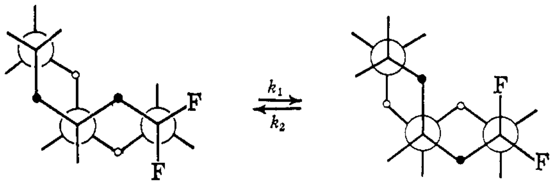
The deductions from the models are in general accord with nmr data. The proton magnetic resonance (pmr) spectrum of *trans*-decalin is a broad multiplet which owes its complexity to extensive spin–spin coupling between the nonequivalent axial and equatorial hydrogens[2] (much like the low-temperature spectrum of cyclohexane[3]) and is consistent with a rigid molecule. In contrast, the pmr spectrum of *cis*-decalin appears to be a reasonably sharp singlet even at −120°.[4a,b] Although this interesting result was initially interpreted to mean that the energy barrier to inversion of *cis*-decalin is very low—possibly less than 6 kcal/mole—the observation is almost surely due to fortuitous near equivalence of the chemical shifts for the axial and equatorial protons of *cis*-decalin.[5]

Although nuclear magnetic resonance spectroscopy has proved exceptionally valuable for conformational analysis and determination of conformational equilibrations, accurate results are often difficult to obtain with systems such as cyclohexane or *trans*-decalin in which complex spin–spin splittings occur. These difficulties can often be alleviated by massive deuteration[6,7] but it is true that the chemical-shift differences of protons in different conformations are often small and, thus, difficult to measure accurately. More dramatic (and accurate) results can usually be obtained by substituting one or more fluorine atoms for hydrogen and observing the fluorine-19 magnetic resonance spectrum.[8] Fluorine chemical shifts are much more sensitive to molecular environment[9] and are usually a factor of 10 to 50 larger than those for protons in similar circumstances.

The chemical-shift difference between the axial and equatorial fluorine-19 resonances of 1,1-difluorocyclohexane is nearly 14 ppm,[10] while the corresponding difference in the proton resonances of cyclohexane is 0.45 ppm.[3] The spectrum of 1,1-difluorocyclohexane is, of course, strongly temperature dependent and study of the variation in the spectrum with temperature indicates an energy barrier to ring inversion of about 10 kcal/mole.[11] This result is in substantial agreement with barriers found using other fluorinated or deuterated cyclohexanes.[8b]

The "fluorine-labeling" technique was used in the present study of the conformational equilibration of several *cis*-decalins. The important idea here, as can be seen from molecular models, is that the *gem*-difluoro group of 2,2-difluoro-*cis*-decalin is expected to flip back and forth between two, magnetically distinct, locations in going from the double-chair form IIIa to the double-chair form IIIb where IIIa and IIIb correspond to the enantiomers of *cis*-decalin (IIa and IIb).





IIIa IIIb

When inversion of 2,2-difluoro-*cis*-decalin is slow we expect to observe two AB quartets in the fluorine magnetic resonance spectrum, one for each conformational isomer. If inversion is rapid, the spectrum should be a single, average AB quartet with but a small chemical shift if IIIa or IIIb are present in roughly equal amounts and a larger chemical shift in either IIIa or IIIb tends to predominate strongly. The reason for expecting a small chemical shift with nearly equal populations is that the fluorine which is axial in IIIa becomes equatorial in IIIb and *vice versa*.

Results

At room temperature, the fluorine spectrum of 2,2-difluoro-*cis*-decalin (III) is a broadened, low-intensity pattern of the AB type with a chemical shift of about 500 cps. As the temperature is progressively lowered, two distinct AB quartets emerge. Several spectra from a typical experiment with III are shown in Figure 1. The particular sample contained 29% of a species which showed a temperature-independent AB spectrum and from its properties was deduced to be the *trans* isomer.

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[2] J. I. Musher and R. Richards, *Proc. Chem. Soc.*, 230 (1958).

[3] F. R. Jensen, D. S. Noyce, C. H. Sederholm, and A. J. Berlin, *J. Am. Chem. Soc.*, **82**, 1256 (1960).

[4] (a) W. B. Moniz and J. A. Dixon, *ibid.*, **83**, 1671 (1961); (b) N. Muller and W. C. Tosch, *J. Chem. Phys.*, **37**, 1170 (1962). The latter authors, operating at 56.4 Mcps, noted small, but apparently real, variations in the spectrum of *cis*-decalin and concluded that ring inversion is slow at −117°.

[5] F. G. Riddell and M. J. T. Robinson, *Chem. Commun.*, 227 (1965).

[6] F. A. L. Anet and M. Z. Haq, *J. Am. Chem. Soc.*, **87**, 3147 (1965).

[7] N. Muller and P. J. Schultz, *J. Phys. Chem.*, **68**, 2026 (1964).

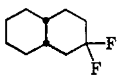
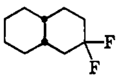
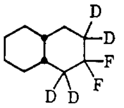
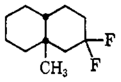
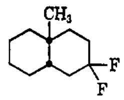
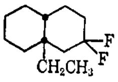
[8] Examples of the use of this procedure are: (a) cyclobutanes (J. B. Lambert and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 3884 (1965)); (b) cyclohexanes (F. A. Bovey, E. W. Andersen, F. P. Hood, and R. L. Kornegay, *J. Chem. Phys.*, **40**, 3099 (1964)); (c) cycloheptanes and cyclooctane (E. S. Glazer and J. D. Roberts, unpublished results presented at the 19th National Organic Symposium of the American Chemical Society, Tempe, Ariz., June 17, 1965).

[9] A. Saika and C. P. Slichter, *J. Chem. Phys.*, **22**, 26 (1954).

[10] K. Nagarajan and J. D. Roberts, unpublished work; see J. D. Roberts, *Angew. Chem. Intern. Ed. Engl.*, **2**, 58 (1963).

[11] J. Jonáš, A. Allerhand, and H. S. Gutowsky, *J. Chem. Phys.*, **42**, 3396 (1965).

Table I. Nmr and Kinetic Parameters for Exchanging *cis*-Decalins

Compound	Solvent	Chemical shift relative to CF_3COOH^a		J_{AB}^a	$E_a^{b,c}$	ΔF^{*b}	ΔS^*, eu^c	%^{d}
		Equatorial	Axial					
 2,2-Difluoro-*cis*-decalin	Acetone a	593	1354	234	15.0 ± 0.9	12.3	8 ± 5	74
	b	528	875	236	14.5 ± 0.9	11.7	8 ± 5	26
 2,2-Difluoro-*cis*-decalin	Propene a	597	1354	233	14.6 ± 0.7	12.2	6 ± 3	74
	b	541	875	239	13.9 ± 0.7	11.6	6 ± 3	26
 1,1,3,3-Tetradeuterio-2,2-difluoro-*cis*-decalin	Propene a	626	1395	236	13.4 ± 0.8	12.4	2 ± 3	74
	b	568	931	240	13.4 ± 0.9	11.8	4 ± 3	26
 9-Methyl-2,2-difluoro-*cis*-decalin	Propene a	451	995	239	9.1 ± 0.6	12.1	−13 ± 3	52
	b	302	699	242	9.2 ± 0.6	12.0	−12 ± 3	48
 10-Methyl-2,2-difluoro-*cis*-decalin	Acetone a	698	1411	235	10.6 ± 0.6	12.8	−10 ± 3	77
	b	470	658	233	10.4 ± 0.6	12.1	−9 ± 3	23
 9-Ethyl-2,2-difluoro-*cis*-decalin	Acetone a	276	834	239	9.5 ± 0.5	11.8	−11 ± 4	50
	b	383	932	236	9.5 ± 0.5	11.8	−11 ± 4	50

[a] In cps. [b] In kcal/mole. Nine to eleven data pairs used for each calculation. [c] Root mean squared errors are appended: J. B Hendrickson, *J. Am. Chem. Soc.*, **83**, 4537 (1961); **84**, 3355 (1962). [d] Per cent of this conformer at 25°.

Since the frequencies and, presumably, the intensities of transitions characteristic of the *trans* material do not change with temperature, they provide a convenient means for estimating the relative intensities of the portion of the spectrum due to the equilibrating *cis* isomer. Theoretical spectra generated by a computer reproduce well the line positions, shapes, and relative intensities of the exchanging species (Figure 1) and permit estimation of the time constants which characterize 2,2-difluoro-*cis*-decalin at various temperatures.

The pairs of lines representing axial and equatorial fluorines have quite different shapes. This is because of couplings involving (primarily) the adjacent protons and is helpful in permitting identification and assignment of each group of resonances in the low-temperature spectrum to axially or equatorially disposed fluorines. The dihedral angle–coupling constant relationship of Karplus appears to apply at least qualitatively to hydrogen–fluorine couplings,[12] and for this reason an axial fluorine is expected to be more strongly coupled to adjacent protons than an equatorial fluorine. The individual lines resulting from these couplings were unresolvable and resulted only in a much greater line width for the axial fluorine resonance (50–60 cps) compared to the equatorial resonance (15–20 cps). Thus, within a given AB quartet, the broad, upfield pair of lines is assigned to the axial fluorine atom and the remaining pair to the equatorial fluorine.

In principle, there are two distinct ways in which the partners of two interconverting sets of AB nuclei may exchange; the A nucleus of one group may become either the A or the B nucleus of the second group. The first possibility is unlikely since it would result only if the ring containing the *gem*-difluoro group stayed while the other ring changed its conformation. The second

$$A(1)\text{–}B(1) \rightleftarrows A(2)\text{–}B(2) \qquad A(1)\text{–}B(1) \rightleftarrows B(2)\text{–}A(2)$$

mode of exchange transforms an axial fluorine atom of one conformation of 2,2-difluoro-*cis*-decalin into the equatorial fluorine atom of the second conformation; only when this latter kind of exchange was assumed was it possible to generate theoretical spectra that agreed with experimental spectra.

Rate constants for inversion of 2,2-difluoro-*cis*-decalin at a given temperature were estimated by adjusting the input parameters for the computer program until a theoretical spectrum superimposable upon the experimental spectrum was obtained. The rate

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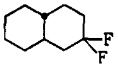
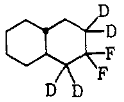
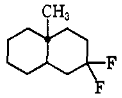
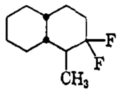
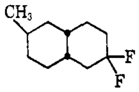
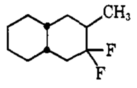
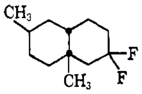
(12) J. B. Lambert and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 3891 (1965).

Table II. Nmr Parameters for Nonexchanging Decalins

Compound	Solvent	Chemical shift relative to CF_3COOH^a Equatorial	Axial	$J_{AB}{}^a$	Temp range investigated, °C	
 2,2-Difluoro-*trans*-decalin[a]	Acetone	684	1341	234	−81 to 51	A
 1,1,3,3-Tetradeuterio-2,2-difluoro-*trans*-decalin[b]	Propene	730	1426	239	−70 to 29	
 10-Methyl-2,2-difluoro-*trans*-decalin[b]	Acetone	651	1238	236	−89 to 86	
 1-Methyl-2,2-difluoro-*cis*-decalin	Propene	1092	2223	238	−25 to 31	B
 6-Methyl-2,2-difluoro-*cis*-decalin	Propene	599	1358	236	−104 to 70	
 3-Methyl-2,2-difluoro-*cis*-decalin	CS_2	1213	2253	242	−66 to 94	
 6,9-Dimethyl-2,2-di-fluoro-*cis*-decalin	Acetone	297	704	241	−104 to 71	

[a] In cps. [b] Examined as an impurity in the *cis* isomer.

constants were fitted to the Arrhenius equation by least squares,[13] and the enthalpy, entropy, and free energy of activation were calculated by standard equations.[14]

10-Methyl-, 9-methyl-, and 9-ethyl-2,2-difluoro-*cis*-decalin, in addition to the parent compound, were found to undergo detectable interconversion. Rate and equilibrium constants for these conformational isomerizations are collected in Table I. On the other hand, with 1-methyl-, 3-methyl-, 6-methyl-, and 6,9-dimethyl-2,2-difluoro-*cis*-decalin only one AB spectrum was observed at each temperature studied; the point of equilibrium between conformers must be so shifted that interconversion has no effect on the fluorine spectrum. Data for these compounds as well as data for several rigid, 2,2-difluoro-*trans*-decalins are summarized in Table II.

Discussion

The calculations which led to the results summarized in Tables I and II involved several assumptions which are common to most studies of this type. In the first place, the input for the computer program by which the theoretical spectra were generated included an "effective" relaxation time, T_2, for each nucleus. These relaxation times were adjusted so as to correspond to the experimental line width (mainly due to H–F coupling) of each resonance at the low-temperature extreme. The same T_2 was then used for calculations at intermediate temperatures. This assumption is not likely to lead to serious difficulty since the spectra are relatively insensitive to small variations in the T_2 values in the intermediate temperature range. Furthermore, when the line widths of the fluorine resonances in 2,2-difluoro-*cis*-decalin were reduced by replacing the protons adjacent to the *gem*-difluoro group with deuterium atoms, the kinetic parameters obtained with the resulting 1,1,3,3-tetradeuterio-2,2-difluoro-*cis*-decalin were nearly

(13) H. Hargenau and G. M. Murphy, "The Mathematics of Physics and Chemistry," D. Van Nostrand and Co., Inc., Princeton, N. J., 1956, p 517.

(14) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, p 71.

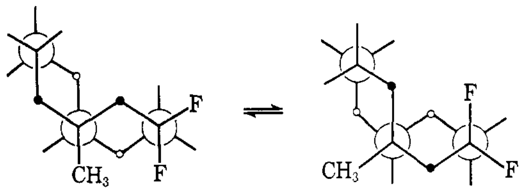
identical with those obtained with nondeuterated material. Thus, the use of an effective relaxation time to take into account the effect of H–F coupling on the theoretical spectra seems to be justified.

We have assumed that the chemical shifts of the fluorine atoms do not change with temperature. Although a slight upfield shift of fluorine resonances with increasing temperature has been noted in other systems,[15] we have observed that, within experimental error, the chemical shifts of the rigid *trans*-difluorodecalins and the apparently rigid substituted *cis*-decalins (Table II) do not change appreciably with temperature. It is, therefore, likely that the chemical shifts of the fluorine atoms in the molecules undergoing measurable exchange are reasonably independent of temperature.

The activation energies and the equilibrium parameters for interconversion of the conformers of 2,2-difluoro-*cis*-decalin do not seem to be solvent dependent, identical results being obtained in acetone and propene. Large solvent effects on these properties of the other molecules studied were assumed to be absent.

Tentative identification of the conformers present in 2,2-difluoro-*cis*-decalin can be made by comparing the entries in Table I for 2,2-difluoro-*cis*-decalin (III), 9-methyl-2,2-difluoro-*cis*-decalin (IV), and 10-methyl-2,2-difluoro-*cis*-decalin. For both conformations of each compound, the fluorine resonances of the equatorial fluorine atom are in the range 500 ± 200 cps upfield from trifluoroacetic acid. The axial fluorine resonances of the conformational isomer of each compound that is characterized by the smaller chemical-shift difference (henceforth called the "b isomer" which corresponds to IIIb) appear in the range 700 ± 175 cps. However, the axial fluorine resonance of the second, larger chemical-shift conformation (the "a isomer" corresponding to IIIa) of 9-methyl-2,2-difluoro-*cis*-decalin is found nearly 400 cps below the corresponding resonances for the unsubstituted and 10-methyl-substituted compounds. This conformation of 9-methyl-2,2-difluoro-*cis*-decalin is destabilized relative to its partner (the relative populations are nearly 1:1) while the relative amounts of both conformers of 2,2-difluoro- and 10-methyl-2,2-difluoro-*cis*-decalin remain at 3:1. Clearly, interaction of an axial fluorine atom with the angular, 9-methyl group at the ring junction is responsible for these effects. By this interaction the magnetic and chemical environments of the axial fluorine atoms in both conformations of 9-methyl-2,2-difluoro-*cis*-decalin are made more similar than in the other compounds studied. This similarity is reflected magnetically in the chemical-shift differences and thermodynamically in the near equality of the amounts of each conformer present. The 10-methyl substituent exerts a smaller effect on chemical shifts and relative conformational populations. The results for each of the inverting difluoro-*cis*-decalins are most mutually consistent if the AB multiplet with the large chemical-shift difference is assigned to the conformational isomer a and the multiplet with the smaller chemical shift to b.

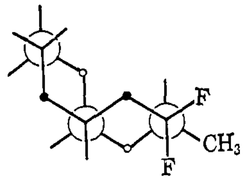
Several factors may influence the chemical-shift differences between the fluorines in the conformations of these compounds. Probably most important is the fact that fluorine atoms are slightly larger than hydrogen atoms and nonbonded hydrogen–fluorine interactions might be sufficient to distort the difluoro-*cis*-decalins away from a perfect, double-chair arrangement of carbon atoms. Distortion of the carbon skeleton could alter the magnetic shielding experienced by the fluorine nuclei and it is possible that fluorine spectra are more sensitive to such distortions than proton spectra. It is interesting to note, in this context, that the chemical-shift difference in 1,1-difluorocyclohexane is over 870 cps (at 56.4 Mcps); this molecule may be closer to a perfect chair conformation.



IVa IVb

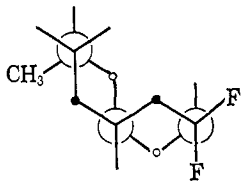
9-methyl-2,2-difluoro-*cis*-decalin

In addition to the incidentally observed spectra of the 2,2-difluoro-*trans*-decalins, several *cis*-decalins gave fluorine magnetic resonance spectra which were independent of temperature (Table II). These latter compounds were substituted with methyl groups at positions other than the ring junction. The F^{19} spectrum of both 3-methyl- and 6-methyl-2,2-difluoro-*cis*-decalin consisted of only one AB multiplet. The appearance of the spectra did not change with temperature. The predominant isomer of both of these methyl derivatives is presumed to be a conformation analogous to the a conformation (IIIa) of 2,2-difluoro-*cis*-decalin—the substantial preference of the methyl for an equatorial disposition for practical purposes "freezing" the molecules into this conformation. The chemical shifts of the 6-methyl derivative were found to be nearly identical with those of conformation a of 2,2-difluoro-*cis*-decalin, showing that a distant methyl group does not exert a strong magnetic effect of its own but acts only to cause a single conformation to be preferred.



Va

3-methyl-2,2-difluoro-*cis*-decalin



VIa

6-methyl-2,2-difluoro-*cis*-decalin

In the preparation of the methyl-substituted difluoro-*cis*-decalins by the reaction of sulfur tetrafluoride with the corresponding ketones, no effort was made to use stereochemically homogenous ketones as regards the relation of the methyl group to the ring junctions and it was surprising that there appeared to be none of the difluoro compounds formed which would exist in a preferred conformation analogous to conformation b of 2,2-difluoro-*cis*-decalin (IIIb). We have no explanation for this and can only suggest that perhaps some subtle steric effect is operative during the reaction of the corresponding decalone with sulfur tetrafluoride.

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[15] R. A. Newmark and C. H. Sederholm, *J. Chem. Phys.*, **43**, 602 (1965).

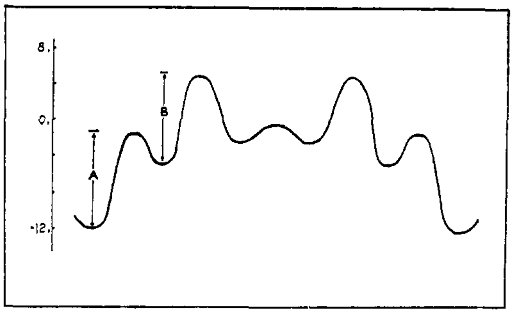


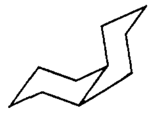
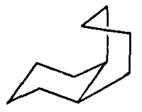
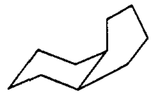
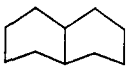
Figure 2. Ordinate, potential energy in kcal/mole; abscissa, reaction coordinate.

Such an effect also appears to operate in the reaction of sulfur tetrafluoride with 6,9-dimethyl-*cis*-decalone-2 because only the isomer corresponding to conformer b of 9-methyl-*cis*-decalone is formed; the carbonyl function is effectively shielded by the 9-methyl group when the ketone is in a conformation analogous to a. Alternatively, isomerization may occur during the reaction with sulfur tetrafluoride.

The process which inverts the *gem*-difluoro group in 2,2-difluoro-*cis*-decalin converts the axial fluorine atom of one environment into the equatorial fluorine atom of the other environment and must involve both cyclohexane rings. If we are to construct a reasonable potential energy diagram for the reaction we must have some idea of the relative stabilities of the chair–chair, chair–boat, and boat–boat conformations of *cis*-decalin.

Geneste and Lamaty have suggested that the preferred ground-state conformation of *cis*-decalin may be a twisted, double-boat form.[16] The suggestion was based on potential energy calculations which included only contributions from H–H bonbonded interactions and the "torsional barriers." The relative energies of the conformations calculated in this way were strongly dependent upon the parameters chosen for the nonbonded interaction potentials. Although electron-diffraction studies of *cis*-decalin are consistent with a double-chair form,[17] it is not clear that the twisted, double-boat was considered during the calculation of the radial distribution functions and, therefore, this configuration cannot be excluded on this basis alone. We have made potential energy calculations for the decalins by Wiberg's method,[18] which takes into account not only H–H nonbonded interactions, but also contributions from C–H and C–C nonbonded interactions, C–C–C and C–C–H bond-angle deformations, and C–C and C–H bond-stretching deformations. While the results are still dependent upon the nature of the potential functions chosen for each interaction, the calculated differences in potential energy between conformations seem to be fairly reliable in other systems.[18] When hydrogen–carbon and carbon–carbon nonbonded interactions are included in the potential energy calculations, the chair–chair form of *cis*-decalin emerges as substantially more stable than any other conformation. Data in support of this conclusion are collected in Table III.

Table III. Potential Energy Calculations for *cis*-Decalin

Conformation	H–H nonbonded[a]	Other nonbonded[a]	Torsional[a]	Total energy[a]
 Chair–chair, I	−3.10	−9.55	0.14	−12.34
 Chair–boat (α), II	10.80	2.60	5.95	20.12
 Chair–boat (β), III	−2.60	−8.70	5.94	−4.96
				
Boat–boat,[b] VI (ε = 0°)	−2.67	−7.84	8.92	−0.55
Boat–boat,[b] V (ε = 33°)	−4.87	−8.29	9.58	−2.83
Boat–boat,[b] IV (ε = 60°)	−2.01	−7.84	11.88	2.78

[a] In kcal/mole. All other energy terms were negligibly small.
[b] ε is the dihedral angle at the ring juncture.[16]

It is possible to construct a plausible energy diagram (Figure 2) for the course of the interconversion of conformers of *cis*-decalin with the aid of the data in Table III. If indeed the most stable form of *cis*-decalin is the chair–chair form, inversion of the rings results most reasonably when the molecule passes successively from the chair–chair to chair–boat to boat–boat conformers. A possible transition state connecting these forms is depicted in Figure 3. As the methylene group at C-3 passes through the plane defined by carbon atoms 1, 2, 4, and 5, eclipsing of methylene groups and C–C–C bond angle deformations are maximum. A similar transition state must obtain during the inversion of cyclohexane. The height of barriers A and B should be roughly equal to the experimental inversion barrier for cyclohexane, 10 kcal/mole,[6] because these barriers result, basically, from the conversion of a chair cyclohexane-like fragment to a boat arrangement. From the diagram in Figure 2 and this estimate, we can deduce that the barrier to inversion of *cis*-decalin should be about 17 kcal/mole—the energy difference between the double-chair and chair–boat forms plus the energy of barrier B. Considering the nature of the several assumptions made, the agreement with the experimental value, 14.0 ± 0.8 kcal/mole, can be regarded as reasonable.

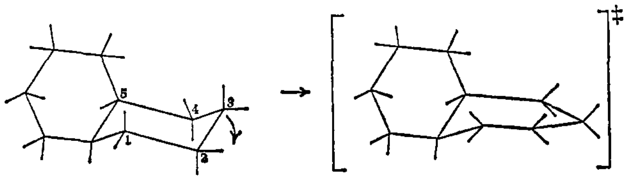


Figure 3. A possible transition state between the chair–chair and chair–boat forms of *cis*-decalin.

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(16) P. Geneste and G. Lamaty, *Bull. Soc. Chim. France*, 2439 (1964).
(17) M. I. Davis and O. Hassel, *Acta Chem. Scand.*, **18**, 813 (1964).
(18) K. B. Wiberg, *J. Am. Chem. Soc.*, **87**, 1070 (1965). The potential functions attributed by Wiberg to Hendrickson (Table I, footnote *c*) were used.

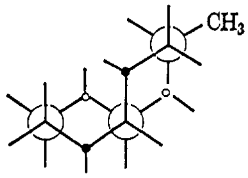
Table IV. Physical Properties of Substituted 2,2-Difluoro-*cis*-decalins

Substituent	Yield, %	Bp, °C (mm)	$n^{22}D$	Purity by vpc	Infrared bands, cm^{-1}
2,2-Difluoro	32	58–59 (7)	1.4484	95[a]	1450, 1360
1,1,3,3-Tetradeuterio-2,2-difluoro	30	66–70 (8)	1.4472	82[b]	2230, 2160, 1480
9-Methyl-2,2-difluoro	15	92–93 (16)	1.4540	95	
10-Methyl-2,2-difluoro	48	73–76 (12)	1.4515	93[c]	1440, 1370
9-Ethyl-2,2-difluoro	42	103–106 (29)	1.4650	88	
1-Methyl-2,2-difluoro	32	71–75 (8)	1.4485	55[d]	1480, 1380
3-Methyl-2,2-difluoro	30	72–75 (7)	1.4421	75	
6-Methyl-2,2-difluoro	28	75–80 (4)	1.4460	90	1490, 1420
6,9-Dimethyl-2,2-difluoro	40	110–114 (19)	1.4559	88	1445, 1360

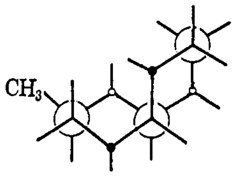
[a] *cis*-Decalone-2 obtained *via* the recrystallized commercial decalol. [b] *cis*-Decalone-2 obtained by the annealation–reduction sequence. [c] Only one resolvable band. [d] At least three components were present.

If *cis*-decalin were to exist primarily in a twisted-boat form (dihedral angle (ϵ) at the ring junction equal to 33°), inversion could take place by rotation about the 9,10 carbon–carbon bond. The double-boat form (ϵ = 0°) would represent a maximum in energy during this process and the barrier to inversion would be estimated to be about 2.5 kcal/mole using our data (Table IV) or 4–10 kcal/mole using the data of Geneste and Lamaty.[16]

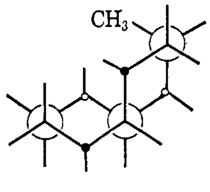
Potential energy calculations were also performed for 3-methyl- (VII) and 6-methyl-*cis*-decalins (VIII) in conformations with axial (a) or equatorial (e) methyl groups. The results are shown below. These calculations suggest that an equatorial disposition of the 3-methyl group is strongly favored over the axial arrangement (IVa). Preference for an equatorial environment is much less pronounced in the 6-methyl derivative. As expected, H–H nonbonded interactions are responsible for most of the calculated energy differences. Once again, the calculations are in qualitative agreement with experiment.



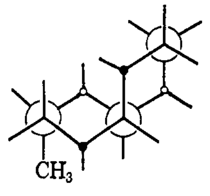
VIIe
E = −13.8 kcal/mole



VIIIe
E = −14.2 kcal/mole



VIIa
E = ~23 kcal/mole



VIIIa
E = −13.3 kcal/mole

An important question relating to the present results with difluorodecalins is the degree to which they can be regarded as pertinent for the corresponding nonfluorine-containing hydrocarbon counterparts. Until reliable nonbonded potential functions for fluorine are available, we cannot be sure. Obviously, if the fluorine atoms in 2,2-difluoro-*cis*-decalin were behaving exactly as hydrogen atoms, then the proportions of conformers a and b would be expected to be equal. In fact, population differences which correspond to 650 cal/mole (or less) difference in thermodynamic stability are observed. Although the ground states of both fluorine-containing conformational isomers are probably raised in energy (relative to *cis*-decalin) by nonbonded hydrogen–fluorine interactions, it seems probable that the results can be extrapolated to the behavior of the parent hydrocarbon.

Experimental Section

The *gem*-difluorodecalins used in this study were prepared by the reaction of sulfur tetrafluoride with the corresponding ketone.[19] The ketones were prepared by previously reported methods or obtained commercially.

Proton magnetic resonance spectra were obtained with a Varian A-60 spectrometer using 20% solutions in carbon tetrachloride. Chemical shifts are reported in parts per million relative to internal tetramethylsilane. Infrared spectra were recorded with a Perkin-Elmer Model 237 spectrophotometer employing films of the neat liquid on sodium chloride plates. Melting and boiling points are uncorrected. A Perkin-Elmer Model 800 chromatograph with flame-ionization detector was used for vapor phase chromatography. Columns composed of Ucon-polar or Carbowax substrates on Chromosorb W support were normally used.

***cis*-Decalone-2** was prepared by catalytic reduction of $\Delta^{1,9}$-octalone-2. The octalone was obtained by annealation of methyl vinyl ketone to cyclohexanone morpholine enamine.[20] The procedure of Augustine was used for reduction; the product was a mixture of *cis* and *trans* isomers in the ratio of 4:1.[21]

Alternatively, the ketone was prepared by chromic acid oxidation of *cis*-decalol-2. The alcohol was prepared by reduction of 2-naphthol at 200 atm with platinum oxide as catalyst.[22] It was found that commercially available "*trans*-decalol-2" (*trans*-decahydro-2-naphthol, Aldrich Chemical Co.) was, in reality, predominantly the *cis* isomer; chromic acid oxidation of the commercial product followed by treatment of the ketonic product with sulfur tetrafluoride gave a product containing 71% 2,2-difluoro-*cis*-decalin. A reasonably pure sample of the *cis* alcohol could be obtained by recrystallization of the commercial product from *n*-hexane.

1-Methyl-*cis*-decalone-2 (Aldrich Chemical Co.) was redistilled before use, bp 119–121° (12 mm) (lit.[23] bp 128–130° (16 mm).

3-Methyl-*cis*(?)-decalone-2 (Aldrich Chemical Co.) was used as received. It is presumed that this material was obtained by reduction of the corresponding octalone (also available from Aldrich) and therefore is predominantly the *cis* isomer.

6-Methyl-*cis*-decalone-2 was synthesized *via* the morpholine enamine of 4-methylcyclohexanone by addition of methyl vinyl

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(19) W. R. Hasek, W. C. Smith, and V. A. Engelhardt, *J. Am. Chem. Soc.*, **82**, 543 (1960).

(20) G. Stork, A. Buzzola, H. Landesman, J. Szmushoviciz, and R. Terrell, *ibid.*, **85**, 207 (1963).

(21) R. L. Augustine, *J. Org. Chem.*, **28**, 152 (1963).

(22) W. G. Dauben, E. Hoeger, and N. K. Freeman, *J. Am. Chem. Soc.*, **74**, 5207 (1952).

(23) D. K. Banerjee, S. Chatterjee, and S. P. Bhattacharga, *ibid.*, **77**, 408 (1955).

ketone and subsequent catalytic reduction. The preparation of 1-morpholino-4-methylcyclohexene-1 was achieved by heating 112 g (1 mole) of 4-methylcyclohexanone (Aldrich), 300 ml of benzene, and 120 g (1 mole) of morpholine at reflux for 15 hr. During this time, the theoretical amount of water was collected by azeotropic distillation. Most of the benzene was removed by distillation at atmospheric pressure. The pressure was then lowered to 20 mm and the residual yellow liquid was distilled, bp 130–136° (20 mm). The proton magnetic resonance spectrum of the material was wholly consistent with the assumed structure.

6-Methyl-$\Delta^{1,9}$-octalone-2. The procedure of Stork was employed.[20] In a 500-ml flask was placed 25 g (0.14 mole) of the above-described enamine, 100 ml of dry dioxane, and 8 g of redistilled methyl vinyl ketone. The mixture was stirred for 1 hr at room temperature, then heated to reflux for 5 hr. After this time, 100 ml of water was added and the mixture was heated under reflux overnight. Another 100 ml of water was added and the mixture was cooled. The resulting red suspension was extracted three times with 100 ml of ether. The combined ether extracts were washed successively with water, 20% hydrochloric acid, water, and saturated sodium chloride solution. The yellow ethereal solution was dried over calcium chloride and concentrated to a small volume. The residue was distilled and gave a major fraction, bp 120–125° (3 mm), amounting to 9.7 g (43%) of nearly colorless liquid ($n^{22}\text{D}$ 1.5158). The infrared spectrum of the material was similar to that of the unsubstituted octalone and had bands at 1730, 1690, and 1640 cm^{-1}.

6-Methyl-*cis*-decalone-2 was prepared by reducing 8 g of 6-methyl-$\Delta^{1,9}$-octalone-2 with hydrogen at 3 atm. Palladium on carbon (10%) was the catalyst; the solvent was 25 ml of absolute methanol containing 1 drop of concentrated hydrochloric acid. After 2.5 hr the theoretical amount of hydrogen had been taken up. The catalyst was removed by filtration and the methanol solution concentrated to a small volume. Fractional distillation of this residue gave one major fraction, bp 105–110° (3 mm), which amounted to 5 g (63%), $n^{22}\text{D}$ 1.4892. The infrared spectrum showed a single, sharp band at 1735 cm^{-1}. Vapor phase chromatographic analysis of the material indicated the purity to be at least 90%; it is assumed that, by analogy to similar reductions,[21] this material is the *cis* isomer. The chemical shifts of the derived difluoride support this assignment.

9-Methyl-*cis*-decalone-2 was prepared by addition of methylmagnesium iodide to $\Delta^{1,9}$-octalone-2 in the presence of cuprous chloride.[24] To a rapidly stirred Grignard solution (19.5 g of methyl iodide (0.14 mole) and 3 g of magnesium metal in 300 ml of absolute ether) was added 0.2 g of dried cuprous chloride (Baker and Adamson reagent). After 15 min, a solution of 12 g (0.08 mole) of $\Delta^{1,9}$-octalone-2 in 25 ml of ether was added dropwise over 30 min. The mixture was warmed to reflux for 20 min and then cautiously decomposed with ice and 20% hydrochloric acid. The ether layer was washed with water and saturated sodium chloride solution followed by drying over calcium chloride. Concentration of the ether afforded a deep yellow liquid. Distillation at atmospheric pressure produced 6.5 g of product, bp 212–215° (lit.[24] bp 250–254°). The proton magnetic resonance and infrared spectra indicated the presence of a small amount of starting octalone; vapor phase chromatographic analysis showed that the material was about 80% pure.

10-Methyl-*cis*-decalone-2 was obtained by the reduction of 10-methyl-$\Delta^{1,9}$-octalone-2. The starting octalone was prepared by the methods of Marshall and Fanta[25] in 14% over-all yield. In 25 ml of absolute methanol containing 1 ml of glacial acetic acid was dissolved 6.1 g of 10-methyl-$\Delta^{1,9}$-octalone-2. Reduction with hydrogen at 3 atm using 10% palladium-on-carbon catalyst proceeded to completion in 45 min. The catalyst was removed by filtration and the filtrate was concentrated. The residue was distilled to give one fraction (5 g, 80%), bp 111–112° (14 mm), $n^{22}\text{D}$ 1.4886. (lit.[26] bp 95–96° (3 mm)). The infrared spectrum showed only a single sharp band at 1690 cm^{-1}. Marshall and Fanta report that vpc analysis of this material gave only one sharp peak. We observe similarly only a single peak, using several different columns. However, it is clear from the ^{19}F spectrum of the derived difluoride that either the ketone contains about 35% of the *trans* ketone or else some isomerization must occur in the sulfur tetrafluoride reaction.

9-Ethyl-*cis*-decalone-2. The procedure was identical with that used for 9-methyl-*cis*-decalone-2 except that ethyl iodide was used in forming the Grignard reagent. The product boiled at 130–135° (30 mm), $n^{22}\text{D}$ 1.5112. The infrared and pmr spectra indicated that the sample was contaminated with some unreacted starting octalone.

6,9-Dimethyl-*cis*-decalone-2. To a Grignard solution prepared from 3 g of magnesium metal and 19.5 g of methyl iodide in 300 ml of ether was added 1 g of dried cuprous chloride (Baker and Adamson). The mixture was stirred for 20 min and then a solution of 12 g of 6-methyl-$\Delta^{1,9}$-octalone-2 was added dropwise. A vigorous reaction ensued and, in about 5 min, a thick yellow precipitate was deposited, leaving a clear, yellow, ethereal solution. Stirring was continued for an additional 2 hr, whereupon the mixture was decomposed with ice and 20% hydrochloric acid. The products were isolated by the procedure used for the preparation of the 9-methyl compound described above. Distillation of the yellow residue gave one fraction, 6 g (~50%), bp 105–120° (12 mm), $n^{21}\text{D}$ 1.5022. Thin layer chromatography on silica gel (cyclohexane elution) indicated only one major component. The infrared spectrum of the material had a sharp band at 1690 cm^{-1}, but also indicated a trace of the starting octalone; the proton magnetic resonance spectra showed a complex system of resonances from 0.9 to 1.0 ppm; these were essentially a superimposition of the spectra of the 6-methyl- and 9-methyl-*cis*-decalones in this region.

1,1,3,3-Tetradeuterio-2,2-difluoro-*cis*-decalin. A small ball of sodium metal was dissolved in 30 ml of deuterium oxide (Columbia Chemical Co.). An equal volume of dry dioxane and 10 g of *cis*-decalone-2 (prepared by reduction of the corresponding $\Delta^{1,9}$-octalone-2) were added and the mixture was stirred for 50 hr. The solution was extracted three times with 50 ml of ether. The combined ether extracts were washed with saturated sodium chloride solution and dried over calcium chloride. After removal of the ether, the residue was distilled to give nearly 10 g of material, bp 122–126° (17.5 mm). The infrared spectrum of the material showed strong bands at 2220 and 2130 cm^{-1}; from the intensity of these bands it was estimated that nearly complete deuteration had taken place at the 1 and 3 positions. The fluorine spectrum of the difluoride derived from the material indicated that it contained 19% of the *trans* isomer.

All 2,2-difluoro-*cis*-decalins used in this study were prepared by the following general procedure. In a 200-ml pressure reaction vessel constructed of Hastelloy C alloy were placed 5 g of the ketone (approximately 0.03 mole), 25 ml of methylene chloride, and 3 ml (0.17 mole) of water. The bomb was sealed and evacuated and then cooled to Dry Ice-acetone temperature and 40–45 g (~0.3 mole) of sulfur tetrafluoride (Matheson Co.) was condensed into the system. The vessel was placed in a Parr rocking apparatus for 12–16 hr at ambient temperature (12 ± 5°). The bomb was then vented and the product of the reaction, a dark, vile liquid, was poured into 50 ml of water. In order to avoid the formation of emulsions during work-up, the methylene chloride solution was triturated with the water. The water was then decanted and a fresh supply was added. This washing procedure was repeated until the decanted water was clear and of neutral pH. The dark methylene chloride solution was dried over calcium chloride and concentrated to about 2 ml. Distillation of this residue at reduced pressure produced, after a small forerun, the desired material in 15–50% yield. Infrared spectra of the reaction products showed that the carbonyl group had been removed and bands in the 1400–1450-cm^{-1} region indicated the presence of carbon–fluorine bonds. The purity of all compounds was checked by vapor phase chromatography. The proton magnetic resonance spectra of these compounds were, in general, singularly uninformative, consisting only of a broad band in the aliphatic region of the spectrum. The fluorine-19 spectra of these materials provided the best evidence that the *gem*-difluoro group had been introduced into the molecule. The physical properties of the 2,2-difluorodecalins prepared for this work are given in Table IV.

Fluorine-19 magnetic resonance spectra were taken with a Varian Associates Model 4300 D spectrometer operated at 56.4 Mcps. Trifluoroacetic acid was used as an internal standard; all resonances appeared upfield from this signal. Spectra were calibrated by audiomodulation of the reference signal. The output of the audio oscillator (Hewlett-Packard Model 200 AB) was monitored by a Hewlett-Packard Model 521 C frequency counter. The resonance pattern was swept in both directions several times in order to minimize effects of drift. The temperature of the sample was controlled by passing a stream of precooled or warmed nitrogen

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[24] A. J. Birch and R. Robinson, *J. Chem. Soc.*, 501 (1943).

[25] J. A. Marshall and W. I. Fanta, *J. Org. Chem.*, **29**, 2501 (1964).

[26] E. C. duFeu, F. J. McQuillan, and R. Robinson, *J. Chem. Soc.*, 53 (1937).

through the sample cavity. Temperatures were monitored by a copper–constantan thermocouple placed above the receiver coil but the actual temperature experienced by the sample was estimated by replacing the sample with a glass tube of similar construction containing another thermocouple.

The temperature of the sample did not vary by more than 1° during a determination and the values given are believed to be accurate to at least 2°. Chemical shifts and coupling constants were determined from low-temperature spectra to an accuracy of at least 1%.

Theoretical spectra were generated by an IBM 7094 II computer (coupled to a Moseley X-Y plotter) using a Fortran IV coded program based on the equations of Alexander.[27] Input to the program included an effective relaxation time, T_2, for each nucleus in the system and mean lifetimes, τ_1 and τ_2, for each AB set of nuclei. The sensitivity of the computed spectra to small variations in the mean lifetimes varied from system to system. However, it is believed that the rate constants so obtained are accurate to 20% or better.

The potential-energy calculations, the results of which are given in Table III, were performed with a slightly modified version of Wiberg's program.[18] No attempt was made to ensure that an absolute minimum had been obtained; the complexity of the system and the amount of computing time required precluded this. The initial structure input to the program had tetrahedral bond angles and equilibrium bond lengths. The structure of the molecule at the first minimum reached did not differ significantly from the original structure.

Acknowledgment. We thank Professor K. B. Wiberg for a copy of his computer program. As part of the freshman honors program, Mr. Gregory Thompson rendered valuable assistance with the synthesis of 9-ethyl-2,2-difluoro-*cis*-decalin.

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[27] S. Alexander, *J. Chem. Phys.*, **37**, 974 (1962).

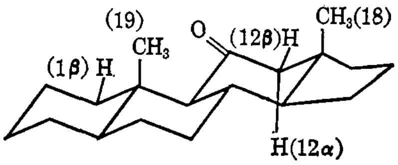
A Variable-Temperature Nuclear Magnetic Resonance Study of Toluene–Ketone Complexes[1,2a]

Pierre Laszlo[2b] and Dudley H. Williams

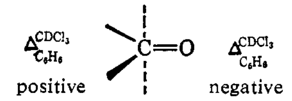
Contribution from the Centre National de la Recherche Scientifique, Institut de Chimie des Substances Naturelles, Gif-sur-Yvette, France, and the University Chemical Laboratory, Lensfield Road, Cambridge, England. *Received January 10, 1966*

Abstract: The temperature variations in the chemical shift of proton resonances in some steroidal ketones in toluene solution have been determined. The changes in resonance positions on passing from an "inert" solvent (carbon tetrachloride) to toluene are accentuated on cooling, since the equilibrium ketone + toluene $\rightleftharpoons$ complex is driven toward complex formation with a decrease in temperature. The temperature variation of the equilibrium constant (calculated in terms of a 1:1 complex) gives the heat of formation of the complex as -0.65 ± 0.15 kcal/mole; in view of the assumptions made in calculating ΔH, this value is probably significant only to an order of magnitude. The sign of solvent shifts induced by toluene relative to carbon tetrachloride closely follows the empirical generalization previously reported for those induced by benzene relative to chloroform.

It has recently been shown[3-5] that benzene solvent molecules can form a stereospecific complex with a ketone group in a solute molecule, in a manner which permits valuable stereochemical and structural conclusions to be made from solvent shift data. The approximate orientation of the complexing benzene molecule with respect to the carbonyl group has been evaluated[5] in the case of 5α-androstan-11-one (I) as solute, on the assumption of a 1:1 benzene–ketone complex. The 11-ketone I offers advantages over other ketones in studies of complexing since the solvent shifts of no less than five protons (18-H, 19-H, 12α-H, 12β-H, and 1β-H), variously oriented with respect to the carbonyl group (see I), can be followed. An empirical correlation has been formulated[3-6] which states that the shift of a proton resonance on passing from deuteriochloroform to benzene solution ($\Delta_{C_6H_6}^{CDCl_3} = \delta_{CDCl_3} - \delta_{C_6H_6}$ ppm) will be positive for protons lying behind a plane drawn at right angles to the C–O bond and passing through the carbonyl carbon atom, but $\Delta_{C_6H_6}^{CDCl_3}$ will be negative for protons lying in front of this plane (see II); protons lying approximately in the plane suffer a very small or zero solvent shift.



I



II

It was now of interest to undertake variable-temperature nmr studies, in the hope of shifting the equilibrium (1) in favor of complex formation and so enhancing the solvent shifts. In addition, the temperature

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[1] Solvent Effects in Nmr Spectroscopy. VII. Part VI: J. H. Bowie, D. W. Cameron, P. E. Schutz, and D. H. Williams, *Tetrahedron*, in press.

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[3] D. H. Williams, and N. S. Bhacca, *Tetrahedron*, **21**, 2021 (1965).

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[5] D. H. Williams and D. A. Wilson, *J. Chem. Soc.*, 144 (1966).

[6] J. D. Connolly and R. McCrindle, *Chem. Ind.* (London), 379 (1965).