929. *Conformational Studies by Nuclear Magnetic Resonance. Part VI.*[1] *Adjacently Deuterated 2-, 3-, and 4-Methylcyclohexanol Esters, Cyclohexyl Nitrite, and Cyclo-octyl Acetate.*

By E. PREMUZIC and L. W. REEVES.

The stereoisomeric mixtures of [2,2,6-$^2H_3$]- and [2,2,6,6-$^2H_4$]-methylcyclohexanols and their acetate esters have been studied. Proton resonance spectra were used to obtain analysis of *cis*- and *trans*-mixtures of adjacently deuterated 2-, 3-, and 4-methylcyclohexanols and their acetate esters. The preferred conformation in each isomer of the alcohols and their esters is shown. The conformation in each molecule was obtained by comparison of chemical shifts and apparent line-widths with similar adjacently deuterated compounds of known conformation.

The proton magnetic resonance spectra of [2,2,6,6-$^2H_4$]cyclohexyl nitrite in carbon disulphide solution have been studied at low temperature. The changes in the spectrum indicate slowing of the chair-to-chair inversion but no evidence of isomerism of the nitrite group has been found.

In the [2,2,8,8-$^2H_4$]cyclo-octyl acetate the apparent line-width of the C-1 hydrogen resonance suggests a similar conformation of the α-CH_2 groups at the C-1 grouping to that of the cyclohexyl acetate at C-1.

SINCE the first report of spectra of locked sugar acetates,[2] the study of saturated ring systems by nuclear magnetic resonance has been followed up from several points of view. Observations of some unlocked six-membered ring compounds at low temperature indicate a resolution in proton magnetic resonance spectra of two distinct rather than rapidly interconverting chair forms.[1a,b] Anet [3] has achieved a simplification of the ring spectrum of cyclohexanol by remote deuteration of the ring methylene groups. The present study is an extension of adjacent deuteration [1d,e] to disubstituted cyclohexanes and examination of cyclohexyl nitrite in comparison to isopropyl nitrite at low temperature. A comparison between [2,2,8,8-$^2H_4$]cyclo-octyl acetate and [2,2,6,6-$^2H_4$]cyclohexyl acetate is also made.

EXPERIMENTAL

Instrumental.—The measurements at room temperature were made on a Varian A60 spectrometer equipped with an audio-oscillator and a Hewlett Packard 522B frequency counter. Chemical shifts were measured with respect to an internal reference of tetramethylsilane (1—2 mol. %). Repeated bracketing of an unknown peak by calibrated side-bands on a sweep width of 50 c./sec., and a sweep time of 500 sec. yielded values reproducible to ±0·1 c./sec. in the worst, and to ±0·5 c./sec. in the best instances.

The variable-temperature experiments were carried out with a Varian H.R. 60 spectrometer equipped with a variable-temperature probe of our own design. All C-1 hydrogen atoms in adjacently deuterated compounds showed shifts of 1 c./sec. to high field on changing from the neat liquids to 5% v/v solutions in carbon tetrachloride. There is a further appreciable solvent shift on replacing carbon tetrachloride with carbon disulphide.[4]

Preparative.—Reduction by lithium aluminium hydride of specifically deuterated ketones yielded the corresponding alcohols. Deuteration of ketones was carried out in basic conditions under reflux with deuterium oxide.[1d] Six exchanges with 99·8% deuterium oxide (Stuart Oxygen Co.) were necessary to obtain ketones containing less than 2% of α-protons. The extent of deuteration was estimated from integrated intensity measurements of proton magnetic resonance spectra measured on a Varian A60 spectrometer. [2,6,6-$^2H_3$]-2-*Methylcyclohexanone*,

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[1] (*a*) Reeves and Strømme, *Canad. J. Chem.*, 1960, **38**, 1241; (*b*) *Trans. Faraday Soc.*, 1961, **57**, 390; (*c*) *J. Chem. Phys.*, 1961, **34**, 1711; (*d*) Premuzic and Reeves, *Canad. J. Chem.*, 1962, **40**, 1870; (*e*) Allan, Premuzic, and Reeves, *ibid.*, 1963, **41**, 204.

[2] Lemieux, Kulling, Bernstein, and Schneider, *J. Amer. Chem. Soc.*, 1957, **79**, 1005; *ibid.*, 1958, **80**, 6098.

[3] Anet, *J. Amer. Chem. Soc.*, 1962, **84**, 1053.

[4] Neikam and Dailey, *J. Chem. Phys.*, 1963, **38**, 445.

b. p. 166—170°; [2,6,6-$^2H_3$]-cis-trans-2-*methylcyclohexanol*, b. p. 165—170°; [2,6,6-$^2H_3$]-cis-trans-2-*methylcyclohexyl acetate*, b. p. 180—182°; [2,2,6,6-$^2H_4$]-3-*methylcyclohexanone*, b. p. 168—174°; [2,2,6,6-$^2H_4$]-cis-trans-3-*methylcyclohexanol*, b. p. 173—178°; [2,2,6,6-$^2H_4$]-cis-trans-3-*methylcyclohexyl acetate*, b. p. 182—184°; [2,2,6,6-$^2H_4$]-4-*methylcyclohexanone*, b. p. 170—171·5°; [2,2,6,6-$^2H_4$]-cis-trans-4-*methylcyclohexanol*, b. p. 170—174·5°; [2,2,6,6-$^2H_4$]-cis-trans-4-*methylcyclohexyl acetate*, b. p. 182—186°;[5] [2,2,6,6-$^2H_4$]-cis-trans-4-*methylcyclohexanol* (2·4 g.), formic acid (6·2 g.), and concentrated hydrochloric acid (1 ml.) were refluxed for three hours. The crude formate was then extracted with ether, washed with saturated sodium carbonate solution and dried over anhydrous sodium sulphate. Pure [2,2,6,6-$^2H_4$]-cis-trans-4-*methylcyclohexyl formate* was isolated by fractional distillation, b. p. 162—166°. [2,2,6,6-$^2H_4$]-Cyclohexanol [1d,e] (5 g.) was added to an aqueous solution of sodium nitrite (4 g.), and the solution cooled to 0°. Concentrated sulphuric acid (2·72 ml.) was then added dropwise for ½ hr., when two layers separated. The upper layer, dried over anhydrous sodium sulphate, was immediately examined spectroscopically. Changes in spectra occur on distillation of cyclohexyl nitrite (b. p. 41°/20 mm.[6,7]) or prolonged standing at room temperature. This is attributed to decomposition and intramolecular changes known to occur in nitrite esters in solution.[8]

[2,2,8,8-$^2H_4$]*Cyclo-octyl acetate*, b. p. 97—103°/21 mm.,[9] was prepared in the usual way.[1d,e]

RESULTS

Fig. 1 shows the spectra of [2,2,6,6-$^2H_4$]-4-methyl cyclohexyl acetate. Spectrum A is complete and indicates peaks at —293·0 and —273·6 c./sec., two peaks at —116·9 and 114·3 c./sec., and a further two peaks at —50·5 and —55 c./sec. (tetramethylsilane reference). These quantities are shown with reduced field-sweep rates in Figs. 1(d), 1(c), and 1(b), respectively. The peaks, shown in Fig. 1(d), are assigned to the C-1 hydrogen in two stereoisomers of [2,2,6,6-$^2H_4$]-4-methylcyclohexyl acetate. Signals in Fig. 1(c) are the corresponding acetate peaks and those in Fig. 1(b) are the methyl signals. The intensity ratios are 1 : 3 : 3. The low-field resonance signals in Fig. 1(e) are due to the formyl protons in [2,2,6,6-$^2H_4$]-4-methylcyclohexyl formate. These also indicate the

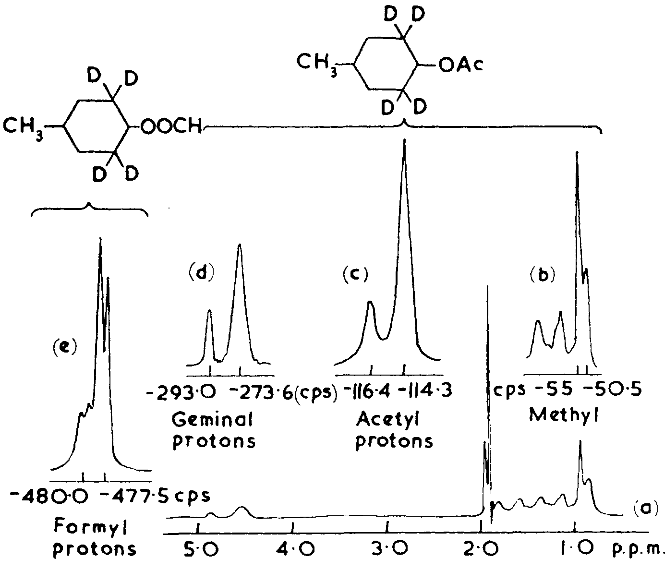

FIG. 1. Spectra of 60 Mc./sec. of [2,2,6,6-$^2H_4$]-4-methylcyclohexyl acetate and formate.

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[5] Heilbron and Bunbury, " Dictionary of Organic Compounds," Eyre and Spottiswoode, London, 1946, Vol. II; " Tables for Identification of Organic Compounds," Supplement to " Handbook for Chemistry and Physics," The Chemical Rubber Publishing Company, Cleveland, 1961.

[6] Soffer, Parrotta, and Di Domenico, *J. Amer. Chem. Soc.*, 1952, **74**, 5301.

[7] Hunter and Marriott, *J.*, 1936, 285.

[8] Kabasakalian and Townley, *J. Amer. Chem. Soc.*, 1962, **84**, 2724.

[9] Jap. Patent 7328/1957 (*Chem. Abs.*, 1958, **52**, 12,908a).

presence of two stereoisomers and some *I–I* interaction with the C-1 proton. Fig. 3(e) shows the C-1 protons' spectrum of the two isomers of 4-methylcyclohexyl acetate. The complex nature of these signals in the absence of adjacent deuteration is evident, although it is still possible in this case to resolve two chemically shifted signals characteristic of the two isomers. The proton resonance spectrum of [2,2,6,6-$^2H_4$]-3-methylcyclohexyl acetate is shown in Fig. 2. Signals for C-1 hydrogen, acetoxyl, and methyl protons are shown at a slower sweep-rate as before. The signals of the methyl protons, shown in Fig. 2(b), are a pair of doublets arising from spin-coupling between the C-3 methyl group and the C-3 protons. Almost equal intensities of the components of the doublets indicate a reasonably large chemical shift between the C-3 methyl and the C-3 proton, compared to the spin–spin interaction between them.[10] The spectra of [2,2,6,6-$^2H_4$]-2-methyl cyclohexyl acetate are illustrated

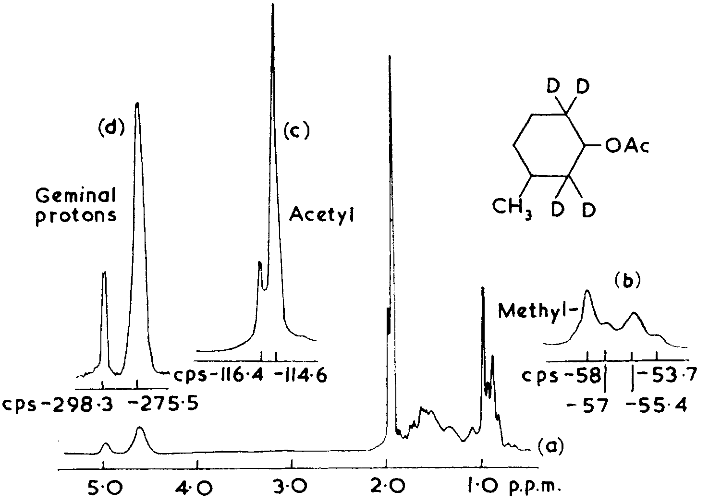

FIG. 2. Spectra at 60 Mc./sec. of [2,2,6,6-$^2H_4$]-3-methylcyclohexyl acetate.

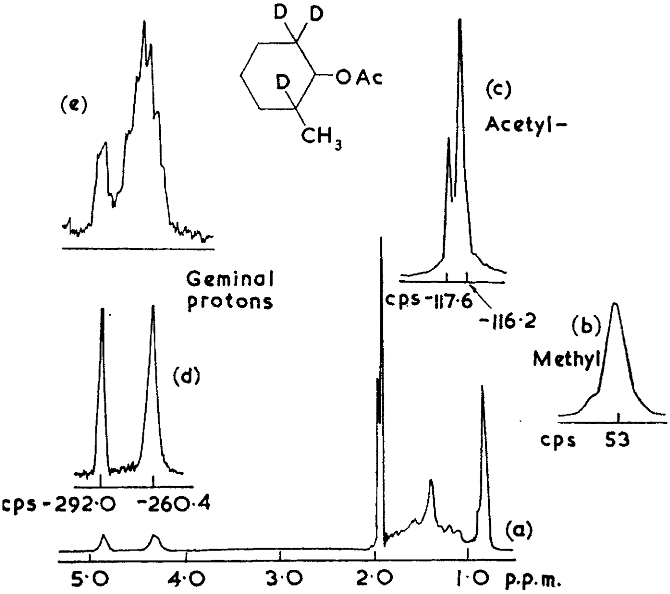

FIG. 3. Spectra at 60 Mc./sec. of [2,6,6-$^2H_3$]-2-methylcyclohexyl acetate: (e) the C-1 hydrogen resonance in 4-methylcyclohexyl acetate.

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[10] Anet, *Canad. J. Chem.*, 1961, **39**, 2262.

in Fig. 3. The C-2 methyl group in the two isomeric forms of this molecule shows almost the same chemical shift. The appropriate chemical shifts and coupling constants are shown in the Table. The assignments of signals to specific stereoisomers will be justified in the discussion.

	cis-Forms				*trans*-Forms				1-Hydrogen ($\delta_{cis} - \delta_{trans}$)
	C-1-Hydrogen		Acetoxyl	Methyl	C-1-Hydrogen		Acetoxy	Methyl	
Compound *	δ †	$\Delta\nu_{1/2}$ ‡	δ	δ	δ	$\Delta\nu_{1/2}$	δ	δ	
[$^2H_4$]-4-Methylcyclohexyl acetate	−293·05	3·7	−116·4	−50·5 ¶	−273·55	7·2	−114·3	−55·0 ¶	19·5
[$^2H_4$]-4-Methylcyclohexyl formate	−302·7	4·2	−480·05 §	—	−282·6	7·4	−477·45	—	20·1
[$^2H_4$]-3-Methylcyclohexyl acetate	−275·5	6·2	−114·6	−57·5	−298·3	3·6	−116·4	−55·4	22·8
[$^2H_3$]-2-Methylcyclohexyl acetate	−292·0	2·8	−117·6	~−53	−260·4	6·1	−116·2	~−53	31·6

* Neat, with internal reference 2% v/v. † C./sec. from tetramethyl silane at 60 Mc./sec. Error ±0·1 c./sec. ‡ C./sec. ± 0·2 c./sec. § Formyl proton. $J = 0·9$ c./sec. between formyl proton and the C-1 proton. ¶ Position of methyl signals due to second-order spectra may be in error systematically [10] in each spectrum.

Samples of deuterated esters were dissolved in carbon disulphide (80% by volume CS_2), and spectra examined at temperatures down to −120°. None of the samples showed any changes in their low-temperature spectra The nuclear magnetic resonance spectra of a 30% solution of [2,2,6,6-$^2H_4$]cyclohexyl nitrite in carbon disulphide show changes in the region of the C-1 proton resonance. This resonance remained a single peak down to −85°, at which temperature the line-width was a maximum, and below this temperature two distinct proton resonance peaks were seen. This is illustrated by the two spectra shown in Fig. 4 taken at −48 and −123°.

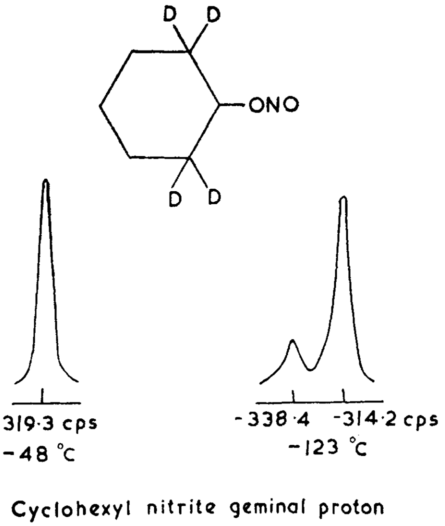

FIG. 4. Spectra of the C-1 hydrogen in [2,2,6,6-$^2H_4$]-cyclohexyl nitrite at two temperatures and 60 Mc./sec.

DISCUSSION

4-Methylcyclohexyl Acetate.—The two stereoisomers of [2,2,6,6-$^2H_4$]-4-methylcyclohexyl acetate are indicated below (I and II), each having two interconverting chair forms, (a) and (b).[1,2,11]

Both I and II are produced on reduction of [2,2,6,6-$^2H_4$]-4-methylcyclohexanone followed by acetylation, the proportions depending somewhat on solvent conditions.

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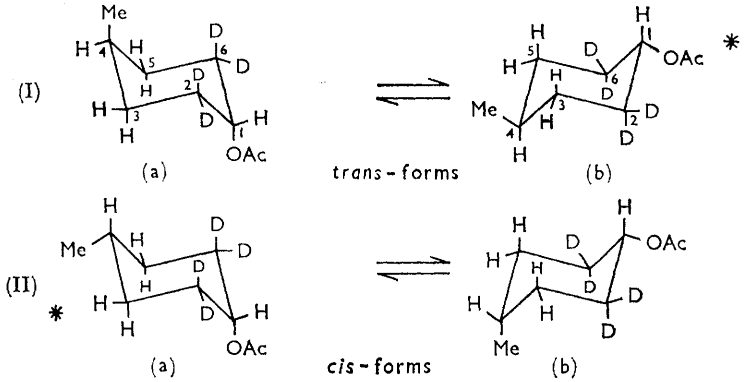
[11] Eliel, Gianni, Williams, Th. H., and Stothers, *Tetrahedron Letters*, 1962, 741; Combe and Henbest, *ibid.*, p. 404.

Reduction by lithium aluminium hydride in ether at room temperature yields 80% of the *trans*-form.[11] Consideration of 3–5 diaxial repulsions in the *trans*-form indicates that almost all the chairs will take up conformation (Ib) with substituents in equatorial positions.[1a,b,11] Consequently, the C-1 hydrogen chemical shift is closely approximated to that in molecule (Ib). In molecule (II) at room temperature we assume, initially, a proton resonance spectrum which is the time-average of forms (a) and (b). The C-1 hydrogen will thus spend an appreciable time in both equatorial and axial positions. Since it is now well established that axial protons are chemically shifted upfield from equatorial protons in the same molecule,[2] and the only difference between (I) and (II) is the orientation of a distant methyl group which is normally neglected,[11] then the higher-field C-1 hydrogen peak in Fig. 1 may be associated with the *trans*-form in which the hydrogen is largely axial. Repeated assessment of relative areas of these two C-1 hydrogen peaks shows that 79·7 ± 1·5% of the mixture is the *trans*-form. This is in excellent agreement with values previously obtained.[11]



It is noted that the axial acetoxyl and C-1 hydrogen resonances are shifted to the high field from the equatorial signals, but the reverse appears to be true with the C-4 methyl groups. The Table gives a list of chemical shifts for the C-1 hydrogen, the acetoxyl and the methyl resonances. Values are also given in the Table for the signal half-widths of the C-1 proton resonance. In the form (Ib), the C-1 hydrogen is axial and thus, to a good degree of approximation, we may take the C-1 hydrogen resonance position as that of an axial C-1 proton geminal to an acetoxyl group. The chemical shift is near that measured by the present authors [1e] for the axial C-1 hydrogen resonance at low temperature in $[2,2,6,6\text{-}^2H_4]$-cyclohexyl acetate (—269·0 c./sec. at 60 Mc./sec.). There is a small shift due to the use of carbon disulphide in the low-temperature work and carbon tetrachloride in the present work. The chemical shift of the C-1 hydrogen in the *cis*-molecule is near that of the equatorial proton signal from the deuterated cyclohexyl acetate (—287·8 c./sec.).

A comparison of $(\delta_{cis} - \delta_{trans}) = 19{\cdot}5$ c./sec. for the two isomers, with $(\delta_e - \delta_a) = 18{\cdot}6$ c./sec. for $[2,2,6,6\text{-}^2H_4]$-cyclohexyl acetate, confirm the occurrence of molecules (I) and (II) solely in the chair forms (Ib) and (IIa). Further evidence is obtained from the lack of any change in spectrum at low temperature in the region of the C-1 hydrogen resonance; thus both stereoisomers prefer one chair form. The limit of detection of forms (Ia) is 3% of (I) and that of (IIb) is 10% of the total (II) in the low-temperature experiment. Similar arguments applied to $[2,2,6,6\text{-}^2H_4]$-4-methylcyclohexyl formate lead to the conclusion that the corresponding chair forms are the only ones present in appreciable amounts.

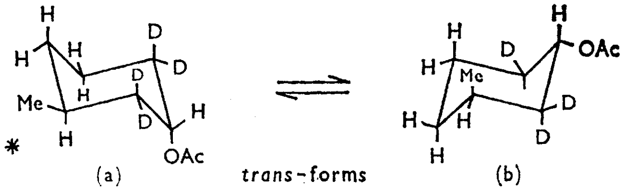
An important feature of the adjacent deuteration technique is that the deuterium resonance on the α-carbons is so far shifted that spin–spin coupling effects enter as first-order splittings.[12] Consider a molecule where the C-1 hydrogen is axial and the 2,2,6,6-positions are fully deuterated. The C-1 hydrogen is coupled to two sets of two equivalent deuterium nuclei. The corresponding proton–proton coupling constants are well known.[3]

Now $J_{a_1a_2} = 11{\cdot}43$ c./sec. in cyclohexanol and $J_{a_1e_2} = 4{\cdot}24$ c./sec. when the C-1 hydrogen is axially oriented, and $J_{e_1a_2} \simeq J_{e_1e_2} = 2{\cdot}71$ c./sec. when the C-1 hydrogen is equatorially oriented. Coupling constants to the 2,2,6,6-deuterium atoms are reduced by a factor $\frac{\gamma\mathrm{D}}{\gamma\mathrm{H}} = 0{\cdot}153$. Thus we can compute values $J_{a_{1\mathrm{H}}a_{2\mathrm{D}}} = 1{\cdot}75$ c./sec., $J_{a_{1\mathrm{H}}e_{2\mathrm{D}}} = 0{\cdot}65$ c./sec., $J_{e_{1\mathrm{H}}e_{2\mathrm{D}}} = 0{\cdot}41$ c./sec. The deuterium nucleus has spin-1-properties; thus two equivalent deuterium atoms cause splitting into five lines of separation equal to J_{HD}. Consequently an axial C-1 hydrogen will appear as a quintuplet, having a separation of 1·75 c./sec., and intensity ratios of 1 : 2 : 3 : 2 : 1. Each of these lines is then further split into five lines having a separation of 0·65 c./sec. Each of these component lines is somewhat broadened by the quadrupolar relaxation[12] so that no individual lines are resolved. A diagrammatically synthesised signal of this type suggests an apparent half-width of 5 to 6·5 c./sec. This is in good agreement with the values presented in this paper for molecules for which other evidence shows an axial C-1 hydrogen.

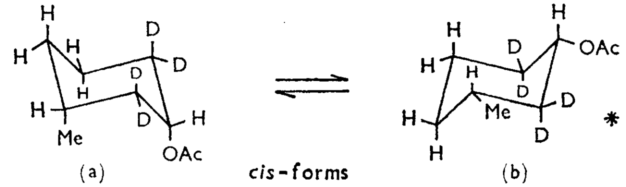
An argument similar to the above, applied to an equatorially oriented C-1 hydrogen between fully deuterated α-carbons, suggests an apparent half-width of 3 to 4 c./sec. Although this cannot be used as a quantitative measure of the preferred conformation, it provides a good indication. For instance, the peaks corresponding to the [$^2H_3$]-2-methyl-derivatives should be slightly sharper, because fewer deuterium nuclei cause splitting of the hydrogen resonance.

3-*Methylcyclohexyl Acetate*.—The two stereoisomers of the deuterated version of this molecule are presented as (III) and (IV) below. The two chair forms of each isomer are present as (a) and (b).

(III)



(IV)



Referring to Fig. 2, and using the same assignments for C-1 hydrogen, acetate, and methyl peaks as before, it is evident that the most abundant isomer in this mixture is the one having predominantly an axial C-1 hydrogen. Since molecule (IVa) can be excluded on steric grounds because of a large methyl-acetate diaxial repulsion, it is evident that the more abundant isomer in the mixture is the *cis*-, existing almost entirely in the (IVb) form. The C-1 hydrogen resonance of the *trans*-form might be assumed to be a time-average of axial and equatorial environment. The magnitude of the chemical shift $(\delta_{cis} - \delta_{trans}) = 22{\cdot}8$ c./sec. between the C-1 protons in the two isomers is detectably greater than $(\delta_e - \delta_a) = 18{\cdot}6$ c./sec. for [$2H_4$]-cyclohexyl acetate at 60 Mc./sec.[1e] This

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[12] Pople, Schneider, and Bernstein, " High-resolution Nuclear Magnetic Resonance," McGraw-Hill Inc., New York, 1959.

suggests that the *trans*-form has the C-1 hydrogen largely in the equatorial position. In the 3-methyl derivatives $(\delta_{cis} - \delta_{trans}) > (\delta_e - \delta_a)$, so that the methyl group at C-3 influences the chemical shift of the C-1 hydrogen to an appreciable extent. The line-widths of the C-1 hydrogen resonances indicate that the *cis*- and *trans*-3-methyl compounds occur in conformations represented by (IVb) and (IIIa). The averaged peak-area measurements showed that the isomeric mixture consisted of 81·4 ± 1% of *cis*-molecules, in agreement with other values for reduction of 3-methylcyclohexanone.[13] The lack of spectral changes with temperature is consistent with the conformations suggested above. Within the limits of spectrometer sensitivity it is evident that, at low temperatures, less than 2% of *cis*-molecules are present as (IVa), and less than 10% of *trans*-molecules as (IIIb).

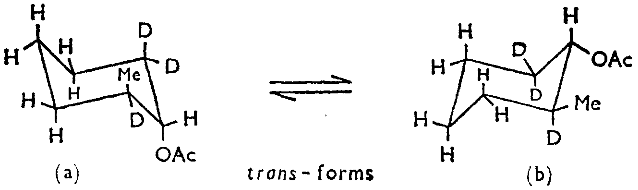
2-*Methylcyclohexyl Acetate*.—The four possible forms of the deuterated version of this molecule are shown below, as (Va), (Vb), (VIa), and (VIb).

The change in the chemical shift of the C-1 hydrogen resonance between the *cis*- and *trans*-2-methyl compounds, $(\delta_{cis} - \delta_{trans}) = 31{\cdot}6$ c./sec., is considerably greater than $(\delta_a - \delta_e) = 18{\cdot}6$ c./sec., the value obtained for [$^2H_4$]-cyclohexyl acetate at 60 Mc./sec.[1e] The C-2 and C-3 methyl groups are sufficiently close to the C-1 hydrogen to affect its chemical shift, the effect being large in the former case. The lack of any change in the spectrum with temperature, and the large change in apparent half-width of the C-1 proton resonances between the *cis*- and *trans*-forms, suggests that at least 96% of *trans*-molecules occur in conformation (Vb), and that at least 93% of the *cis*-molecules prefer the (VIa) conformation.

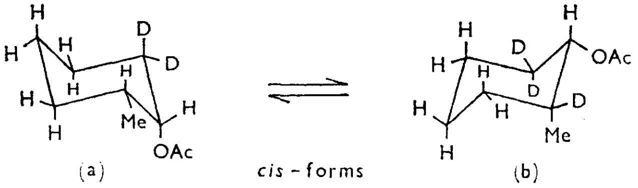
It is interesting to note that in (II), (III), and (VI) the chair-form with the acetate group axial is preferred by at least 90% or more of the molecules. The main repulsions which occur in the axial position are associated with C-3 and C-5 axial hydrogen atoms. The relation of these repulsions to the methyl and the acetate groups is undoubtedly governed by the C-1 oxygen atom of the acetate group. Although the acetate group is the larger, the C-1 oxygen is the important steric factor in this repulsion. However, this atom is smaller than the methyl group, and therefore these repulsions will affect the methyl more seriously than the acetate group. The importance of the C-1 oxygen 3–5 hydrogen repulsions has been suggested in an earlier Paper[1e] which showed that the population of axially oriented ester groupings depended very little on the particular ester.

Relative-area measurements of the C-1 hydrogen peaks in the spectra of the *cis*- and *trans*-forms showed that the mixture contained 66·9 ± 1% of the *trans*-molecules.

(V)



(VI)



[2,2,6,6-$^2H_4$]*Cyclohexyl Nitrite*.—Isopropyl nitrite and all other alkyl nitrites studied previously [14,15] have shown the phenomenon of hindered rotation about the O–N bond. In low-temperature studies by nuclear magnetic resonance, spectra of a general nitrite " RONO " showed two environments for the C-1 protons in " R." These two resonances

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[13] Dauben and Bozak, *J. Org. Chem.*, 1959, **24**, 1596.

[14] Piette and Anderson, *J. Chem. Phys.*, 1959, **30**, 899.

[15] Pietter, Ray, and Ogg, *J. Chem. Phys.*, 1957, **26**, 1341.

correspond to the *cis*- and the *trans*-forms of the nitrite esters. Careful studies[14] have shown that the nuclear magnetic resonance transition temperature in isopropyl nitrite is around -40 to $-46°$, and the energy barrier is about 6·0 kcal. The [*cis*-] : [*trans*-] ratio has been reported[14] to be of the order of 16. The assignment of the methine hydrogen resonances has been questioned, and this ratio may well be an inverted one from the correct value.[16] Dielectric measurements indicate a [*trans*-]:[*cis*-] ratio of 4·26 for isopropyl nitrite and 2·57 for cyclohexyl nitrite in the liquid state at 25°.[17]

In our experiments we expected two transition temperatures in the nuclear magnetic resonance spectrum: one corresponding to nitrite-group isomerisation,[14] and the other to chair-inversion.[1a] Only one transition temperature of $-85°$ is observed, which is considerably lower than that for the nitrite isomerisation. The difference in chemical shift below the transition temperature (24·2 c./sec. at 60 Mc./sec.) is quite similar to that found in other esters of cyclohexanol,[1e] $(\delta_e - \delta_a) = 18{\cdot}5$ c./sec. at 60 Mc./sec. for the acetate, 22·4 for the formate, and 21·5 for the trifluoroacetate and nitrate. The chemical-shift difference for the methine hydrogen in isopropyl nitrite between the *cis*- and *trans*-forms is 45 c./sec. at 60 Mc./sec. This evidence clearly points to the fact that the isomerisation observed by us is the chair-inversion process. The low-field peak at -123 c./sec. was assigned to an equatorial proton and the higher-field peak to an axial proton.[1a,b,c] A mean value for 18 spectra of the relative areas of the two peaks at low temperature indicated $68 \pm 3\%$ equatorially oriented nitrite groups. The chemical shifts at low temperature were measured in carbon disulphide. For comparison with carbon tetrachloride solutions at room temperature, a solvent shift of 7·8 c./sec. was added. At room temperature the signal half-width of the C-1 proton is 5·5 c./sec. The absence of spectra for the two possible isomers of cyclohexyl nitrite in the axial and equatorial position indicates one of the following: (a) one form of the nitrite, presumably the *cis*-form, is seriously sterically hindered in the axial and equatorial position: this is contrary to dielectric evidence;[17] (b) the energy barrier for nitrite isomerisation is much lower in the cyclohexyl compound than in other alkyl nitrites; (c) the signals of the nitrite isomers in low abundance are appreciable but below the noise level in our spectra. Thus in the axial position, the *cis*-form has less than ~10% of the axially oriented nitrite group, and less than ~5% of the equatorially oriented group. Both figures suggest disagreement with the dielectric measurements[15] and with previous nuclear magnetic resonance data on isopropyl nitrite.[14]

Cyclo-octyl Acetate.—It is of some interest to measure the apparent half-width of the C-1 hydrogen resonance of [2,2,8,8-$^2H_4$]cyclo-octyl acetate in comparison to half-widths of the C-1 hydrogen resonance of [$^2H_4$]cyclohexyl compounds of known conformation. The apparent half-width of the C-1 hydrogen resonance in cyclo-octyl acetate is 5·6 c./sec., indicating that the C-1 hydrogen spends about 80% of the time in an environment where the coupling of two of the four vicinal deuterium atoms involves an angle ϕ approaching 180°.[18] The chemical shift of the C-1 hydrogen in [2,2,8,8-$^2H_4$]cyclo-octyl acetate is $-289{\cdot}4$ c./sec. at a concentration of 10% by volume in carbon tetrachloride. An axial C-1 hydrogen in 4-methylcyclohexyl acetate has a chemical shift $-273{\cdot}6$ c./sec. (the Table, *trans*-form) while the axial C-1 hydrogen in [2,2,6,6-$^2H_4$]cyclohexyl acetate at low temperature in carbon disulphide[1e] has a chemical shift -269 c./sec. The C-1 hydrogen in [2,2,6,6-$^2H_4$]-*cis*-cyclohexyl acetate has a chemical shift $-293{\cdot}0$ c.p.s. (the Table), which is close to that in cyclo-octyl acetate.

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