Conformational interconversion of 3,3,5,5-tetramethylmethylenecyclohexane and related compounds

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The proton magnetic resonance spectra of compounds **1** to **4** have been studied at various temperatures. The spectral changes observed for **2**, **3**, and **4** are interpreted in terms of interconverting chair conformations.

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Introduction

Fascinating investigations have been concerned with the determination of the stable conformation of six-membered cyclic compounds (1, 2). In these endeavors numerous techniques, theoretical and experimental, have been used to approach conformational problems from different points of view. From such studies it has emerged that the chair form is highly favored for cyclohexane and that severe constraints, usually in the form of sp^2 hybridized carbon atoms (3), bulky axial substituents (4), and in some cases heteroatoms (5), must be present in the ring to make the twist-boat form more stable than the chair.

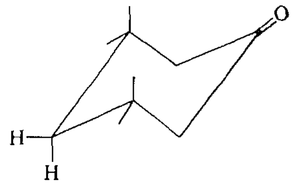
It has long been accepted that 3,3,5,5-tetramethylcyclohexanone (**1**) exists in a chair conformation (6) even though there are severe 1,3-*syn*-axial interactions between methyl groups estimated at about 3.7 kcal/mole (7) and comparable to the energy of the twist-boat form of cyclohexanone calculated to be about 3.5 kcal/mole (8).

Experimental evidence as a result of an X-ray analysis showed that 2,6-dibromo-3,3,5,5-tetramethylcyclohexanone and 2-bromo-3,3,5,5-tetramethylcyclohexanone existed as deformed chairs in the solid state (9). Recent calculations by Allinger (8) predict a greater stability (about 3.8 kcal/mole) for the chair.

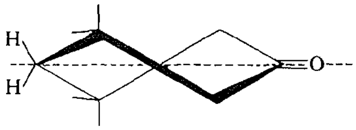
In spite of these overwhelming results supporting a chair form, it has been suggested that the apparently structurally analogous molecule 3-phenyl-3,5,5-trimethylcyclohexanone appears to exist in a twist-boat conformation (8, 10).

Motivated by these apparently conflicting results, it seemed of interest to apply the dynamic nuclear magnetic resonance (d.n.m.r.) method (2) to increase our understanding of the conformational characteristics of **1**. A recent review (2) shows that this approach has met with considerable success in understanding such problems.

A close examination of the chair (c.) and twist-boat (t.b.) conformations suggests that the appearance of the proton magnetic resonance (p.m.r.) signal of the methylene group on carbon-4 (C-4) could supply information on the nature of the stable conformation of **1**. Other t.b. forms need not be considered because of excessive methyl repulsion.



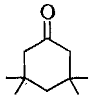
c.



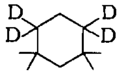
t.b.

In other words it was expected that if conformational interconversions for **1** could be slowed down on the n.m.r. time scale, the low temperature p.m.r. signal of the methylene group on C-4 would either be an AB quartet for c. because of the difference in chemical shifts of the axial (a) and equatorial (e) protons, or be an A_2 singlet for t.b. since the two-fold axis of symmetry through C-1 and C-4 make both methylene protons equivalent. The methyl and α-methylene protons would be of no evident use since the same appearance is expected for these signals for both conformations.

Unfortunately conformational interconversion for **1** like that for cyclohexanone (11) could not be slowed down sufficiently, even at −170 °C, to obtain the p.m.r. spectrum of the stable conformation of **1**. This molecule is therefore not amenable to a d.n.m.r. investigation. Fortunately, however, the recent observation (11) that the replacement of the carbonyl group in cyclohexanone by a methylene group markedly raises the energy barrier to ring inversion suggested that a similar modification of **1** might enable us to achieve our objective. We therefore prepared compounds **1** to **4** for our variable temperature p.m.r. investigation.



1



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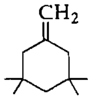

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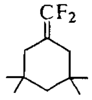


4

Compound **2** was prepared to serve as a model for the others as will be explained in detail later. Molecules **2**, **3**, and **4** showed temperature dependent p.m.r. spectra, the results of which will now be described.

Results and Discussion

(1) 1,1,3,3-Tetramethylcyclohexane-4,4,6,6-d_4 (2)

The starting material **1** was prepared as described by Chiurdoglu and Maquestiau (12). Refluxing **1** with a solution of 10% potassium carbonate in deuterium oxide gave 3,3,5,5-tetramethylcyclohexanone-d_4. Conversion to the tosylhydrazone and reduction with lithium aluminum hydride yielded **2** (13).

The 100 MHz p.m.r. spectra of **2** are shown in Fig. 1 at various temperatures with deuterium decoupling. At ambient temperature the decoupled spectrum consists of three singlets: 0.92 (methyl groups), 1.15 (methylene group on C-2), and 1.49 p.p.m. from internal TMS (methylene group on C-5). The assignment of the respective methylene peaks is based on the results of deuterium decoupling and the p.m.r. spectrum of the non-deuterated compound. As the temperature is lowered a spectral change takes place such that at −135 °C both methylene peaks have changed into AB quartets while the methyl groups now show a doublet of equally intense lines. The coalescence temperatures are estimated at −94 °C for the C-5 methylene AB quartets and −97 °C for the methyl doublet.

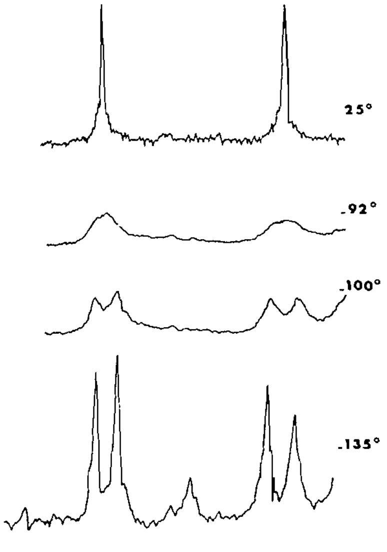


FIG. 1. The 100 MHz p.m.r. deuterium decoupled spectra of the ring protons of **2** at several temperatures. The scale is in p.p.m. relative to internal TMS.

From the spectrum at −135 °C it is possible to determine that the methyl peaks are separated by 10.8 ± 0.2 Hz while the chemical shift difference ($\Delta\nu$) for the protons on C-5 is 11.7 ± 0.5 Hz and the coupling constant is $J = 13.7 \pm 0.5$ Hz. It is apparent that the upfield and downfield AB components of the C-5 and C-2 methylene groups are essentially superposed. Even though the upfield AB component of the C-2 methylene is not visible, it is nevertheless possible to determine that $J = 14.0 \pm 1.0$ Hz and $\Delta\nu = 14.3 \pm 1.0$ Hz.

Using the equation given by Kurland and coworkers (14) one obtains the rate constant (k) for the process responsible for the coalescence of the AB quartets. Eyring's equation (15) then gives the free energy of activation ($\Delta F^{\ddagger} = 8.5 \pm 0.3$ kcal/mole) at −94 °C for the process. A transmission coefficient of $\frac{1}{2}$ has been used; this value will be explained later. Analogically $\Delta F^{\ddagger} = 8.7 \pm 0.3$ kcal/mole was calculated using the rate constant equation given by Pople *et al.* (16) for the coalescence of the methyl doublet at −97 °C.

The presence of two AB quartets in the p.m.r. spectrum at −135 °C proves unambiguously that **2** exists in the chair form with axial and equatorial

TABLE 1

Summary of free energy barriers for cyclohexane and some *gem*-dimethylated cyclohexane derivatives

Compound	$\Delta F^{\ddagger a}$ (kcal/mole)	Reference
Cyclohexane	10.3	18
1,1-Dimethylcyclohexane	10.2	19
1,1,3,3-Tetramethylcyclohexane	8.7	This work
1,1,4,4-Tetramethylcyclohexane	11.1	20

[a]These values are for the chair-to-boat process.

protons of different chemical shifts at positions 2 and 5. This conclusion is in agreement with calculations by Allinger *et al.* (17) which predict c. to be more stable than t.b. by 4.78 kcal/mole.

Knowing that **2** exists in the c. form, immediately identifies the interconversion process as ring inversion, and assuming a mechanism analogous to cyclohexane, a transmission coefficient of $\frac{1}{2}$ was used in the calculation of $\Delta F^{\ddagger}$ above which therefore represents the free energy barrier for the chair-to-boat process (18).

Table 1 contains a summary of $\Delta F^{\ddagger}$ values for cyclohexane and some *gem*-dimethylated cyclohexane derivatives. It is interesting to note that one *gem*-dimethyl group has essentially no effect on the barrier and that two groups in a 1,4-relationship raise it by about 1 kcal/mole while two groups in a 1,3-relationship lower it by about 1 kcal/mole.

The value of $\Delta\nu = 14.3$ Hz for the methylene group on C-2 serves as a model for the next section where an analogous splitting would be expected for the methylene group on C-4 of **3** and **4** if these compounds exist as c. forms unless unusual effects associated with the presence of an sp^2 hybridized carbon are present.

(2) 3,3,5,5-Tetramethylcyclohexanone and Derivatives

Compound **3** was prepared from **1** by a Wittig reaction using the procedure of Greenwald and co-workers (21); **4** was also prepared from **1** by the method developed by Fuqua and co-workers (22).

The 100 MHz p.m.r. spectra of **3** at various temperatures are shown in Fig. 2. Above −100 °C the spectrum consists of three singlets: one at 0.93 (methyl groups), a second at 1.26 (methylene group on C-4), and the third at 1.87 p.p.m. (methylene groups on C-2 and -6). The vinyl methylene singlet is not shown. As the temperature is lowered only the α-proton peak undergoes a spectral modification whereby the singlet becomes an AB quartet below −110 °C, the coalescence temperature. Spectra taken down to −165 °C showed a slight broadening of the other two singlets with respect to the TMS peak but no further splitting was observed. The vinyl proton peak also remained unchanged throughout this temperature interval.

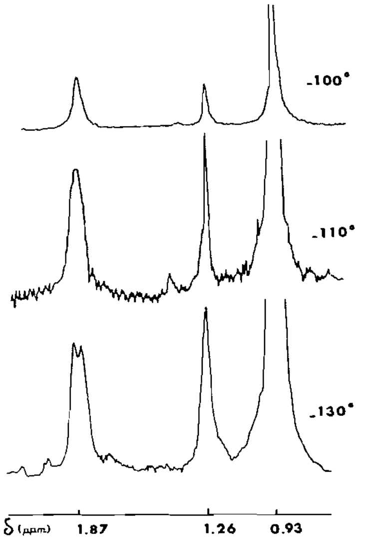


FIG. 2. Upfield portion of the 100 MHz p.m.r. spectra of **3** at several temperatures.

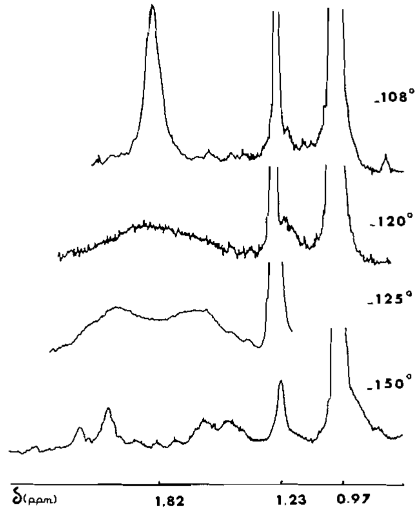


FIG. 3. The 100 MHz p.m.r. spectra of **4** at several temperatures.

The 100 MHz spectra of **4** as a function of temperature are shown in Fig. 3. The high tem-

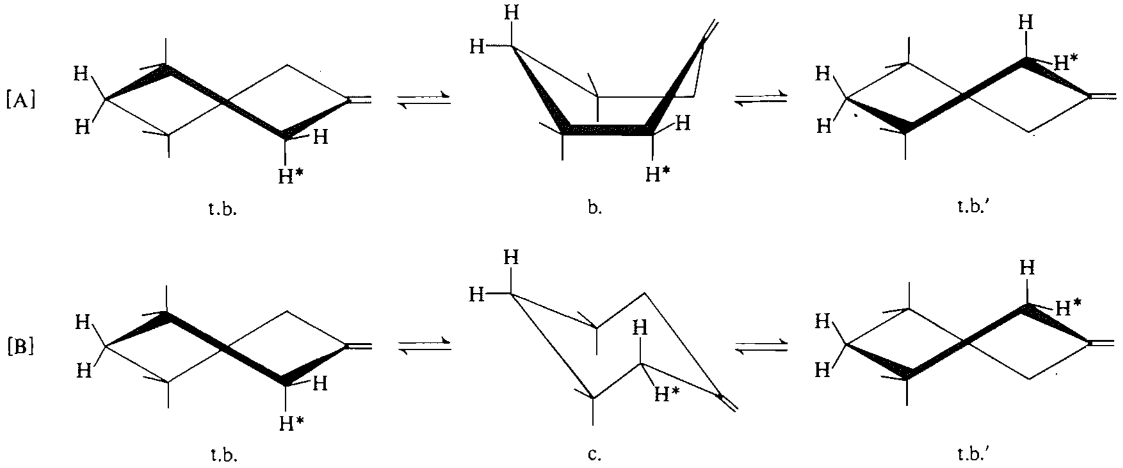


FIG. 4. Pseudorotation (A) and ring inversion (B) itineraries for the t.b. conformation of **1**, **3**, or **4**.

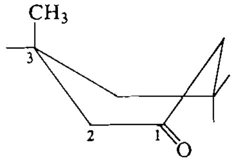
perature spectrum consists of three singlets: one at 0.97 (methyl groups), the second 1.23 (methylene group on C-4), and the third at 1.82 p.p.m. (methylene groups on C-2 and -6). At +25 °C, the last peak actually appears as a triplet (separation 2.2 Hz) because of coupling with the fluorine atoms. As for **3** only the α-proton peak undergoes a spectral change into an AB quartet below −120 °C, the coalescence temperature. The other peaks remained unsplit down to −165 °C. The upfield components of the AB quartet show a marked broadening with respect to the lower field components undoubtedly because of larger $^4J_{HF}$ values.

Spectral parameters for **3** were found to be $J = 13.0$ Hz and $\Delta\nu = 10.5$ Hz while those for **4** were $J = 12.5$ Hz and $\Delta\nu = 57.6$ Hz. The error in these parameters is about 0.5 Hz because of the broadness of the lines. From the equation given by Kurland and co-workers (14), k was obtained from each spectral change and the following $\Delta F^{\ddagger}$ values were calculated using a transmission coefficient of one: 7.9 ± 0.3 kcal/mole for **3** at −110 °C and 7.2 ± 0.3 kcal/mole at −120 °C for **4**.

It is immediately evident from the low temperature spectra of each of **3** and **4** that the multiplicity observed does not satisfy the symmetry requirement of either the c. or the t.b. forms. To be in agreement with c., the methyl singlet should be a doublet while the singlet due to protons on C-4 should be an AB quartet. On the other hand, agreement with the t.b. conformation would require a methyl doublet and a C-4 methylene singlet. There must therefore exist some accidental equivalence of chemical shifts of protons in different molecular environments. It is difficult *a priori* to say conclusively which conformation comes closer to satisfying the requirements of the low temperature spectra. It is possible to demonstrate, however, that the c. form best rationalizes the barriers to conformational interconversion determined from the spectral changes.

If we begin our argument by assuming that the conformational energies calculated (8) for the c. and t.b. forms of **1** are essentially correct, then c. is more stable than t.b. by about 3.8 kcal/mole. Calculations for methylenecyclohexane (23), cyclohexanone (8), cyclohexane and 1,1,3,3-tetramethylcyclohexane (17) indicate that 4 kcal/mole represents a reasonable estimate of the greater stability of the c. form of **3**. The process of conformational interconversion with $\Delta F^{\ddagger} = 7.9 \pm 0.3$ kcal/mole, responsible for the spectral change of **3**, would then be ring inversion analogous to cyclohexane (18) and involving a c. ⇄ t.b. ⇄ c.′ pathway (the prime represents an inverted conformation), where t.b. is a metastable intermediate. We may now deduce that the maximum barrier to pseudorotation (24) of the t.b. form should be no more than about 4 kcal/mole to be compatible with energy profiles constructed from the estimated energy difference between c. and t.b. and $\Delta F^{\ddagger}$ determined from the spectral change.

If, on the other hand, we assume as a working hypothesis that **3** exists in the t.b. form, then two basic modes of interconversion are available, namely a ring inversion and a pseudorotation. Both processes, shown in Fig. 4, have the property of averaging the different types of protons of **3** such that the p.m.r. spectrum at high temperature be in agreement with that given in Fig. 2. If it can be shown that the barrier to pseudorotation should be less than the observed $\Delta F^{\neq}$, then it will follow that **3** cannot exist in the t.b. form, otherwise the spectral change depicted in Fig. 2 should be observed at much lower temperatures. Since the height of the pseudorotation energy profile is either of two possible boat forms, b., shown in Fig. 4 and **5**, their conformational energies relative to t.b. will now be estimated.



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Strain energy minimization calculations not having been done for all conformations of **1** or **3**, maximum conformational energies relative to t.b. will be estimated by the simplest method. As a starting point we shall use results derived for the various boat forms of cyclohexanone (8) and then consider the effect of replacing hydrogen atoms by methyl groups on the basic skeleton. The energies for differently located methyl groups are taken as those calculated for cyclohexane by Hendrickson (25); these values will be used as such and modifications due to the presence of an sp^2 carbon on methyl repulsive interactions will be considered later.

The energy increment of the t.b. skeleton energy of cyclohexanone due to the presence of the four methyl groups arises essentially from two methyl interactions on C-3 and C-5, the sum estimated to be about 2 kcal/mole (25). The difference in conformational energies of the t.b. forms of cyclohexanone and **1** relative to their respective c. forms is calculated as about 0.5 kcal/mole (i.e. 3.78–3.26) (8), thus indicating that the effect of the methyl groups is greater in t.b. than in c. for **1** by about 0.5 kcal/mole. A fair estimate of the 1,3-*syn*-dimethyl interaction in the chair form of **1** is some 3.5 kcal/mole (8); it may therefore be concluded that 2 kcal/mole represents a minimum energy increment due to the presence of methyl groups. This value will be used since it will lead to maximum conformational energy values for b. and **5**, as desired.

The energy of the b. form is made up of 2.2 kcal/mole associated with the cyclohexanone skeleton and the energy of a 1,3-*syn*-dimethyl interaction, not estimated by Hendrickson, but expected to be some 3.5 kcal/mole or less. We may therefore say that 5.7 kcal/mole certainly represents the maximum energy possible for the b. form. Conformation **5** comprises essentially a skeleton contribution of 1.1 kcal/mole and a C-3 methyl interaction of about 3 kcal/mole leading to an energy of 4.1 kcal/mole. Since the replacement of a carbonyl group by an exo-methylene group is expected to lower the skeleton of b. relative to t.b., we can safely say that 3.5 kcal/mole represents a *maximum* value for the conformational energy of either b. or **5** for **3** *relative* to t.b. (taken as 0 kcal/mole), and therefore represents the *maximum* pseudorotation barrier. Even a more generous estimate of 6 kcal/mole would still mean that the spectral change observed for **3** should not occur at the observed temperatures, but at much lower temperatures. It therefore appears highly improbable that t.b. is the predominant conformation of **3** in solution, and, without specifying whether b. or **5** is the barrier height to pseudorotation, the maximum estimate made above is within the maximum limit deduced earlier from calculations and the observed $\Delta F^{\neq}$. Similar arguments are applicable to **4**.

The $\Delta F^{\neq}$ values determined for **3** and **4** are therefore most reconcilable with the c. form. The conformational process would then be ring inversion involving a c. $\rightleftarrows$ t.b. $\rightleftarrows$ c.′ itinerary. It is evident from Fig. 4 that this ring inversion averages the AB quartet of the α-protons to a singlet. It also appears more than likely that **1** should also exist in the c. form, although this cannot be demonstrated other than by analogy with **3** and **4**.

It is interesting to speculate as to the origin of the accidental equivalence of the axial and equatorial methyl groups and the protons on C-4. It appears that the anisotropy of the $=CH_2$ or $=CF_2$ groups is not responsible since it is very different for each substituent as reflected by the Δν of the α-protons of **3** and **4**. It seems possible that the flattening of the ring caused by the introduction of an sp^2 carbon might account for

TABLE 2

Summary of free energy barriers for cyclohexanone, 3,3,5,5-tetramethylcyclohexanone, and their derivatives

Compound	$\Delta F^{\ddagger a}$ (kcal/mole)	Reference
Cyclohexanone	<5.0	11*a*
Methylenecyclohexane	8.4	11*b*
Difluoromethylenecyclohexane	6.8	27
1	<5.0	This work
3	7.7	This work
4	7.0	This work

[a] These values are for the chair-to-boat process. That is, a transmission coefficient of $\frac{1}{2}$ is used in the calculation of $\Delta F\ddagger$ instead of 1.

a large part of this phenomenon. Such a proposition finds precedence in the calculations (26) recently reported where similar effects are attributed in part to the flattening of the ring in t-butyl derivatives of cyclohexane.

Our results then suggest that the presence of the 3,3,5,5-tetramethyl moiety in **1**, **3**, and **4** does not lead to a change in basic conformation with respect to cyclohexanone and its corresponding derivatives. Moreover the free energy barriers are very similar for both classes of compounds as illustrated in Table 2.

The trends observed appear to reflect the trend found for the energy barriers to rotation about C_{sp^2}—C_{sp^3} bonds (28). As suggested for methylenecyclohexane (11), this behavior may be considered as indicative of an appreciable participation of the sp^2 carbon atom in the "flip" to reach the transition state for ring inversion.

Experimental

Infrared (i.r.) spectra were recorded on a Beckman IR-8 spectrophotometer, the sample being a thin film between sodium chloride plates. Mass spectra were obtained on a Hitachi-Perkin-Elmer mass spectrometer model RMU 6-D at 70 eV. Vapor phase chromatography (v.p.c.) analyses were carried out on an Aerograph A90-P3 instrument on 5 ft long, $\frac{1}{4}$ in. diameter columns described later. Carbon, hydrogen analyses were obtained by Midwest Microlab, Inc., Indianapolis, Indiana, U.S.A.

The p.m.r. spectra were recorded on a JEOL JNM-4 H-100 spectrometer operating at 100 MHz using solutions from 2 to 8% of the samples in a mixture of vinyl chloride and chlorodifluoromethane, m.p. −159.9 and −160 °C respectively. The freon was added for field-frequency locking purpose. Compound **1** was investigated as a 3% solution in chlorodifluoromethane alone, however. A small quantity of tetramethylsilane was added and the samples were degassed and sealed (18). Temperatures were monitored by means of a JEOL temperature control unit model JES-VT-3 and read off a calibration chart obtained with a thermocouple inside a dummy n.m.r. tube. Checks on the accuracy of the calibration curve were made repeatedly and are believed accurate to within ±2 °C. Deuterium decoupling was effected by means of the JEOL Hetero Spin Decoupler model JNM-SD-HC.

3,3,5,5-Tetramethylcyclohexanone-2,2,6,6-d_4

Compound **1** (34.0 g, 0.22 moles) (12) was refluxed with a solution of 10 g of potassium carbonate in 100 ml of deuterium oxide for 24 h. The product was then extracted with ether and dried with anhydrous magnesium sulfate. After evaporation of the ether, peak integration on the p.m.r. spectrum revealed essentially 50% deuteration. By repeating the above procedure three times it was possible to obtain 32 g (94%) of the ketone deuterated, essentially 99% as revealed by the complete absence of the peak due to the α-protons.

1,1,3,3-Tetramethylcyclohexane-4,4,6,6-d_4 (2)

Compound **2** was prepared following a sequence of known reactions (13). The deuterated ketone (0.990 g, 0.0062 moles) from the above exchange reaction and 1.20 g of tosylhydrazine were dissolved in 20 ml of hot absolute ethanol. The solution was left standing at room temperature for 24 h. The precipitated tosylhydrazone (1.75 g, 79%) was filtered and used in the next step. Uncorrected m.p. 162–164 °C.

The above tosylhydrazone (0.341 g, 0.00104 moles) was refluxed for 24 h with 0.575 g (0.15 moles) of lithium aluminum hydride in 25 ml of tetrahydrofuran. After hydrolysis of the mixture with 10% sulfuric acid, an extraction with petroleum ether was carried out. The organic solution was then washed with a 5% sodium hydroxide solution and several times with a saturated sodium chloride solution until neutral. Traces of water were removed with magnesium sulfate and the ether was distilled.

The v.p.c. analysis on a column of β,β′-oxydipropionitrile (13% on chromosorb P, HMDS, 60–80 mesh) gave two peaks corresponding to 72% of **2** at 10 min retention time and 28% of 3,3,5,5-tetramethylcyclohexene-2,6,6-d_3 at 11 min. These retention times were identical with those for nondeuterated products which are known substances (12).

Extraction of the concentrated petroleum ether solution with a saturated silver nitrate solution removed most of the olefin. Preparative v.p.c. gave a sample of **2** of purity greater than 98%. A sample of 8% of this compound in a mixture of vinyl chloride and chlorodifluoromethane (9:1, v:v) containing a little TMS was prepared for the low temperature p.m.r. study.

3,3,5,5-Tetramethylmethylenecyclohexane (3)

Following the method described by Greenwald (21), 4.92 g (0.033 moles) of **1** were reacted to yield **3**. Samples for analyses were purified by preparative v.p.c. on carbowax 20M (20% on chromosorb P, HMDS, 60–80 mesh). The i.r. and p.m.r. analytical date were in agreement with those reported in the literature (29). A 5% solution in a mixture of vinyl chloride and chlorodifluoromethane (9:1, v:v) containing a little TMS was prepared for the low temperature p.m.r. study.

3,3,5,5-Tetramethyldifluoromethylenecyclohexane (4)

Following the method described by Fuqua (22), 4.62 g

(0.030 moles) of **1** were reacted to yield **4**. Samples for analyses were purified by preparative v.p.c. on a carbowax 20M column. Mass spectrum, molecular ion at m/e = 188; i.r. 1758 ($C{=}CF_2$); p.m.r. (7% in a mixture of $CH_2{=}CHCl$: CHF_2Cl, 9:1, v:v), 0.97 (singlet, CH_3), 1.23 (singlet, CH_2), 1.82 p.p.m. (triplet, separation 2.2 Hz, α-CH_2).

Anal. Calcd. for $C_{11}H_{18}F_2$: C, 70.18; H, 9.64. Found: C, 70.18; H, 9.81.

A 2% solution of **4** in a mixture of vinyl chloride and chlorodifluoromethane (9:1, v:v) containing a little TMS was prepared for the low temperature p.m.r. study.

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