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THE CONFORMATIONAL EQUILIBRIUM OF 1,3-DICHLORO-5-METHYLCYCLOHEXANE

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Abstract—Two of the stereoisomers of the title compound were prepared and their dipole moments were measured. For the *r*-1,*c*-3-dichloro-*t*-5-methylcyclohexane, the free energy difference between conformers with axial–axial (aa) and equatorial–equatorial (ee) chlorines was measured by a variable temperature NMR method, and the value found was $1.3 \pm 0.2\ \mathrm{kcal/mol^{-1}}$ (in acetone) favoring the latter. Molecular mechanics studies show that the solvation energy and the electrostatics are of major importance in understanding this equilibrium. Calculations show the effect of the methyl group is essentially additive, and give for *cis*-1,3-dichlorocyclohexane itself $ee \rightleftharpoons aa$ $\Delta H +$ $3.0\ \mathrm{kcal\ mol^{-1}}$ (acetone).

The conformational preferences in the halogenocyclohexanes have been investigated extensively[1,2] due to the relative ease of obtaining reliable experimental data, and to the insight which such determinations give on the stereochemistry, interatomic interactions and reactivities in these and more complex molecules. There are however, few reports of studies on compounds in which there are interactions between groups in 1,3-disubstituted cyclohexanes. Such interactions may have important effects on conformational equilibria. The 2-halocyclohexanones,[3] for instance, exhibit a preference for the axial halogen, while in the *cis*-2,6-dihalocyclohexanones, the diequatorial conformers are more stable than the diaxial ones.[4]

Not much effort has previously been directed toward the synthesis of 1,3-dihalocyclohexanes, perhaps in part because of the fact that the conversion of 1,3-cyclohexanediols to dihalides yielded mixtures of isomers.[10] The 1,3-dichlorocyclohexanes have been obtained in small yields in mixtures resulting from the chlorination of chlorocyclohexane[5] or cyclohexene.[6] They were separated by preparative vpc[7] and their mass spectra were analyzed.[8,9] The amounts of these compounds in mixtures of dichlorocyclohexanes were studied by ^{13}C-NMR.[5]

The 1,3- and 1,4-dibromocyclohexanes (mixtures) have been prepared,[10] from the corresponding cyclohexanediols. The compounds were separated by column chromatography and by glc, and their conformations were assigned on the basis of dipole moments and spectral data.

Attempted measurements of the diequatorial–diaxial equilibria in the *cis* isomers of both 1,3-dibromo-[10] and 1,3-dichlorocyclohexane[5] failed to detect the diaxial conformations, thus making it impossible to determine the energy difference between conformations, which would have given quantitative information on the intramolecular halogen–halogen interactions in these molecules. It was thought that the large syn-axial repulsion between the halogens in the 1,3-dichloro compound might be approximately compensated by an axial C-5 methyl group on the cyclohexane ring. This might then put the conformational equilibrium into a measurable range. In this paper we report the synthesis and the study of the conformational equilibrium in *r*-1,*c*-3-dichloro-*t*-5-methylcyclohexane. The compound was prepared from orcinol (3,5-dihydroxytoluene) which was hydrogenated to a mixture of diols, followed by conversion of the diols to the corresponding dihalides, as is shown in Fig. 1. (All chiral compounds discussed are *dl*-mixtures, but one enantiomer is shown.)

THE REACTION SCHEME

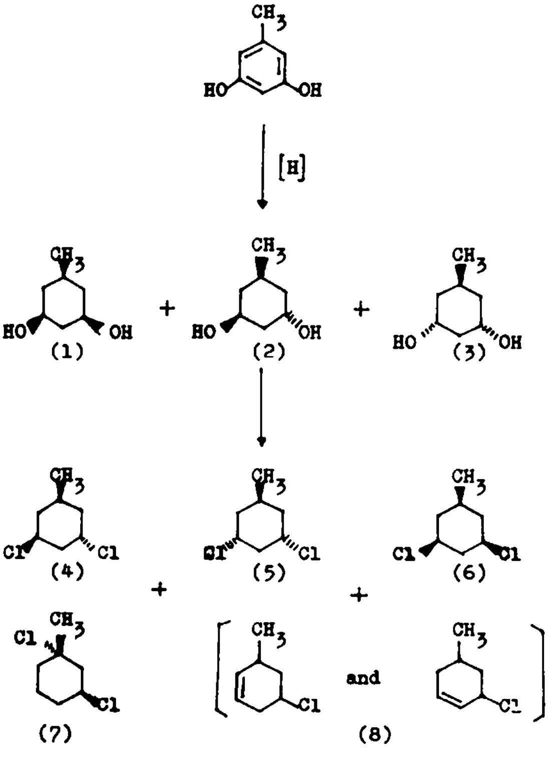


Fig. 1. The reaction scheme.

Synthesis, isolation and structure determination of the isomers of 1,3-dichloro-5-methylcyclohexane

Hydrogenation of orcinol monohydrate with Rh/Al_2O_3, PtO_2 or Raney nickel leads to a mixture of cyclohexanediols. With Raney nickel, all three possible isomers (**1**–**3**), were obtained. With Rh/Al_2O_3 only **1** and **2** were obtained in about equal amounts, while PtO_2 produced **1** accompanied by small amount of **2**. The last procedure was accompanied by hydrogenolysis, however, and yielded only 32% of total diols.

Orcinol monohydrate has been hydrogenated with Rh/Al_2O_3[11] and with Raney nickel,[12] and the products have been isolated from the reaction mixture by fractional crystallization with 30%[11] and 20%[12] overall yields of diols. We found that distillation of the reaction mixture resulting from hydrogenation with Rh/Al_2O_3 yielded 85% of the mixed diols, which could be further separated if necessary.

Assignment of the configuration of the 5-methyl-*r*-1,*t*-3-cyclohexanediol was carried out by Agosta and Schreiber[11] on the basis of the IR and NMR data. Our isomer **2** is identical with this compound on the basis of NMR and IR spectra and melting points, as well as on the fact that the C-1 and C-3 proton signals in the NMR differ in both position and width (i.e. coupling constants).

The mass spectra of the 5-methyl-1,3-cyclohexane diols, as well as their chemical ionization mass spectra,[13] have been previously discussed.[12] The configuration of the *t*-5-methyl-*r*-1,*c*-3-cyclohexanediol and *c*-5-methyl-*r*-1,*c*-3-cyclohexanediol have been assigned on the basis of ^{1}H-NMR data which have been announced[14] but not yet published.

According to the m.ps, our isomer **1** is identical to the *c*-5-methyl-*r*-1,*c*-3-cyclohexanediol, whereas **3** is identical to the *t*-5-methyl-*r*-1,*c*-3-cyclohexanediol. The configurations were confirmed by NMR, where resonance of the C-1, C-3 protons appears at higher magnetic field in the case of isomer **1**, which is consistent with the axial orientation of these protons in the dominant conformer of this isomer.

Furthermore, the high dilution IR spectrum of **1** in CCl_4 between 3000 and 4000 cm^{-1} records only one band at 3645 cm^{-1}, corresponding to the free OH vibration, while for isomer **3** two bands are recorded, one at 3650 cm^{-1} corresponding to the free OH vibration, and another one at the 3570 cm^{-1} corresponding to the intramolecular hydrogen-bonded OH vibration. The ratio of the band intensity at 3570 cm^{-1} to the band intensity at 3650 cm^{-1} did not change upon further dilution. This supports the conclusion that both OH groups in isomer **3** are axial, and internally hydrogen bonded in part.

The fact that the retention time of **3** on FFAP or Carbowax glpc columns is smaller than that for **1** or **2**, due to deactivation of the diaxial OH groups by the intramolecular hydrogen bond, is consistent with the configurational assignments.

Conversion of alcohols to alkyl halides with $SOCl_2$ in pyridine is known to proceed without rearrangement and with inversion of configuration.[5] This substitution in the sugar moiety[16] of nucleosides[17] with Ph_3P/CCl_4 proceeded mainly with inversion of configuration, while the reaction of Ph_3P and *N*-bromo-, or *N*-chloro- succinimide resulted in complete inversion of configuration, for instance in 3α-, and 3β-cholestanol and 5α-androstane-3-ol-17-one.[18] It was reasonable to expect that in the reaction of a mixture of **1** and **2**, a mixture of *r*-1,*t*-3-dichloro-5-methylcyclohexane **4** and *r*-1,*c*-3-dichloro-*t*-5-methylcyclohexane **5**, would be obtained, with the latter being desired for the present work. Two isomers were indeed obtained, both of which gave correct carbon, hydrogen and chlorine analyses and molecular weights for $C_7H_{12}Cl_2$, substantiating the predicted cyclic structures. For both of these, mass spectra showed a low intensity molecular ion *m/e* 166, 168, 170, confirming the existence of two chlorine atoms in the molecule. The cracking patterns of these isomers are similar to other dihalocyclohexanes,[8] having a base peak at *m/e* 95, corresponding to $C_7H_{11}^+$. Loss of a hydrogen chloride molecule followed by loss of a chlorine atom appears to be the favored process, although loss of two hydrogen chloride molecules is also important. The abundance of the M^+-HCl peak in the mass spectrum of **4** compared with the much smaller abundance of this peak in **5** suggests that **4** has one chlorine atom in the axial position.

The assignment of the configuration of isomer **4** is straightforward from the ^{1}H-NMR spectrum. A doublet at δ 0.98 is due to the (CH_3–CH) methyl group. The low field multiplets at δ 4.30 and δ 4.50 originate from two different protons on the chlorinated carbons 1 and 3, the first being axial and the other equatorial. Because of the appreciable 1,3-syn-axial interactions between methyl and chlorine,[19] this isomer has the time-average properties of a rigid molecule existing in the conformation with the equatorial methyl group. Absorptions at δ 2.61 and δ 2.38 in the spectrum of this isomer together represent one proton and have the appearance of the low-field portion of an AB quartet (J_{gem} = 13.8 Hz). These peaks are assigned to the equatorial C-2 proton. The corresponding axial C-2 proton resonance overlaps resonances of the other protons.

In the ^{1}H-NMR spectrum of the isomer assigned structure **5**, a doublet at δ 1.02 is observed representing the three protons of the (CH_3–CH) methyl group. The low-field multiplet at δ 4.02 originates from two axial protons on the chlorinated carbons. The position of the signal,[25] and the large coupling constant (J_{ax-ax} = 11 Hz) which is observed together with the smaller one (J_{ax-eq} = 5 Hz) are consistent with axial orientations of these protons. Absorptions at δ 2.77 and δ 2.58 originate from the same proton and correspond to the low-field portion of an AB quartet (J_{gem} = 11.4 Hz), which is assigned to the equatorial C-2 proton.

The possibility that this compound is in fact *r*-1,*c*-3-dichloro-*c*-5-methylcyclohexane, isomer **6**, is ruled out by the ^{13}C NMR spectrum. The assignments of carbons in the ^{13}C-NMR were deduced on the basis of signal multiplicity[20] in the off-resonance decoupled ^{13}C NMR spectrum. The assignment of the configuration is straightforward on the basis of additivity rules[20] from the carbon shifts given in the Table 1.

The predominantly equatorial orientation for the chlorine atoms in isomer **5** was also deduced from the NMR spectrum (Table 1). The conformation of the methyl group, which is the only difference between isomers **5** and **6**, was also established from the ^{13}C-NMR spectrum. The observed chemical shifts in Table 1 agree with the calculated shifts of the 1,3-dichloro-5-methylcyclohexane conformer with the equatorial chlorines and axial methyl group, while they differ considerably from the values calculated for the isomer with the equatorial chlorines and an equatorial methyl group, or for isomer **6**. This permits assignment of the *r*-1,*c*-3-dichloro-*t*-5-methylcyclohexane structure to the isomer **5**, and the

Table 1. ^{13}C-NMR shifts of the 1,3-dichloro-5-methylcyclohexane isomers

carbon	observed shifts isomer (5)	calculated shifts[a] (5)		(6)[b]
		ee	aa	ee
1,3	53.6	53.9	54.3	60.3
2	46.5	49.3	41.1	49.1
4,6	41.4	41.7	42.3	45.3
5	28.6	28.7	21.3	33.3
CH_3	18.4	19.9	23.9	23.9

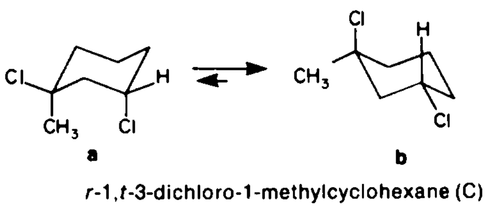
a) ee-conformation with equatorial chlorines, aa-conformation with axial chlorines; b) the aa conformation of (6) was disregarded.

predominant conformation with the chlorines equatorial.

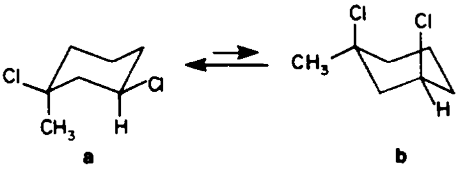
The mass of compound **7**, obtained from the reaction of a mixture of diols **1** and **2** with hydrogen chloride, does not show a molecular ion. This is probably due to the very easy loss of hydrogen chloride, indicative of an axial orientation of one C–Cl bond and its position on a tertiary carbon atom. The *m/e* 130, 132 (M^+-HCl) peak contributes only 3% to the mass spectrum of the compound, and *m/e* 95($C_7H_{11}^+$) is the base peak, as of the other dihalocyclohexanes.

In the NMR spectrum of **7** a singlet at δ 1.63 originates from the three protons of the (CH_3–CCl) methyl group. The low-field signal at δ 4.18 (H–C–Cl) is a triplet of triplets and represents one proton. The values of the coupling constants ($J_{ax-ax} = 11$ Hz and $J_{ax-eq} = 5$ Hz) require the predominantly axial orientation of this proton. The position and shape of the signal are very similar to those of the corresponding signal in compound **4**. Absorptions at δ 2.60 and δ 2.42 originate from the C-2 proton, but the AB pattern is not clearly observed because of overlapping with other signals.

There are two possible configurations that may be assigned to compound **7** on the basis of the IR, NMR, and mass spectral data (C and D). A choice between these cannot be convincingly made from the available data.



r-1,*t*-3-dichloro-1-methylcyclohexane (C)



r-1,*c*-3-dichloro-1-methylcyclohexane (D)

Results of dipole moment and conformational energy measurements

In order to obtain more information regarding the structures of the 1,3-dichloro-5-methylcyclohexanes, the dipole moments of compounds **4** and **5** were determined by measuring the dielectric constants and densities of solutions of the compounds **4** in *n*-hexane, and of compounds **4** and **5** in CCl_4, at 20°C. Molar polarizations at infinite dilution ($P_{2\infty}$) were calculated by the method of Halverstadt and Kumler,[21] and the orientation polarizations were in turn calculated utilizing the index of refraction measurements at the D-line. Atomic polarization was neglected. The dipole moments were calculated from the Debye equation.

Table 2 gives the calculated dipole moments for the possible conformations of **4** and **5**, as well as the observed dipole moments.

As expected, the dipole moments of **4** and **5** are similar and the calculated values are in a good agreement with those experimentally observed. The calculated dipole moment of **5** with both chlorine atoms equatorial is almost identical with the experimental one. Therefore, the predominant conformation of isomer **5** is the one with equatorial chlorines, which is consistent with the NMR results (below).

The low temperature NMR spectra of isomer **5** were recorded for the compound in solution in both $CDCl_3$ and in deuterated acetone (Fig. 2). As the temperature goes down, the proton spectrum goes from sharp to broad to sharp again, but no new bands appear. There must be a small amount (probably at least 0.5%) of the minor component present at −45°, or the bands would not change in the way observed. On the other hand, as much as 10% should show some separate bands strong enough to identify.

Strictly speaking the C-1(C-3) proton signal is a complex one. It was, however, possible to obtain an exact ($J_t + J_c$) value since the spectral pattern is a distinct triplet of triplets (Fig. 2). The values of ($J_t + J_c$) were 15.01 ± 0.12 Hz and 16.05 ± 0.12 Hz at 29° and −75° respectively.

$$J_t = n_{ee}J_{aa} + n_{aa}J_{ee}$$

$$J_c = n_{ee}J_{ae} + n_{aa}J_{ea}$$

We can write:

$$n_{ee} = 1 - n_{aa} = [(J_t + J_c) - (J_{ea} + J_{ee})]/[(J_{aa} + J_{ae}) - (J_{ea} + J_{ee})]$$

where n_{aa} and n_{ee} are the fractions of the *aa* and *ee* conformers and J_{aa}, J_{ee}, J_{ae}, J_{ea} are the corresponding coupling constants. An analysis of this type on a very similar system has been reported.[23] The value ($J_{aa} + J_{ae}$) = 16.0 ± 0.25 Hz may be determined from the signal of an axial C-1(C-3) proton of the *r*-1,*t*-3-dichloro-5-methyl-

Table 2. Observed and calculated dipole moments

Compounds	$\mu^{a}_{obs.}$ (D)	$\mu^{d}_{calc.}$ (D)
(4)	$2.2\pm0.1^{b}, 2.27\pm0.01^{c}$	2.60
(5) Cl aa	$2.48\pm0.01^{c,f}$	3.77
(5) Cl ee		2.56

(a) all at 20°C; (b) n-hexane; (c) CCl_4; (d) IDME method, ref. 22

(f) dipole moment of the compound itself

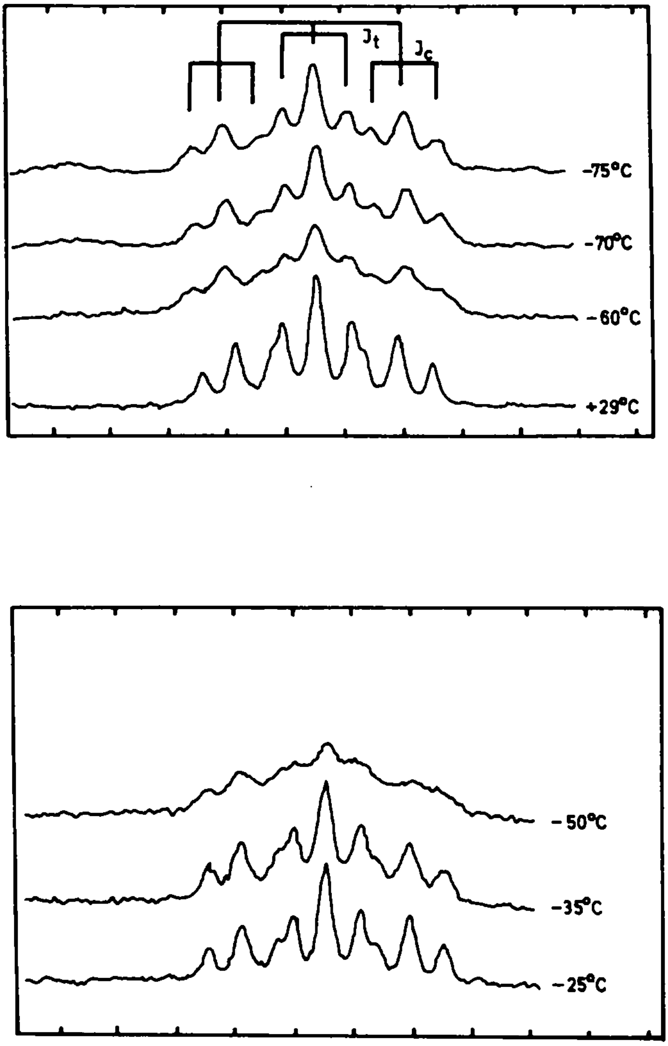


Fig. 2. The low temperature ^{1}H NMR spectra of isomer 5, in acetone (above) and in deuterochloroform (below).

cyclohexane 4 which exists in a fixed conformation with the methyl group equatorial. Following the procedure of Booth[24] the 2/3 band width of the equatorial C-1(C-3) proton of the isomer 4 ($= J_{ea} + J_{ee}$) was 7.5 ± 0.5 Hz. The energy difference $\Delta E_0^a(E_{aa} - E_{ee})$ was estimated by minimizing φ, at two different temperatures (29°, −75°), in the following equation:

$$\Phi = \sum_T [J - n_{ee}(J_{aa} + J_{ae}) - n_{aa}(J_{ee} + J_{ea})]^2$$

where $J(= J_t + J_c)$ is the observed value at the temperature T. The ΔE_0^a was determined to be 1.3 ± 0.2 kcal/mole.

The chloroform data are less complete because the solvent freezes near the coalescence point, but confirm the above in general.

An alternative interpretation of the data is possible. If we note the value of $(J_t + J_c)$ increases with decreasing temperature, and that $(J_t + J_c)$ becomes equal to the value for $(J_{aa} + J_{ae}) = 16.0$ at −75°, then it may be that we are observing the pure *ee* conformation, while the signals from the *aa* conformation, because of the low concentration of the latter, are lost in the base line. In that case only the spectrum at 29° can be used to determine the conformational energy from the equation:

$$n_{ee} = 1 - n_{aa} = ((J_t + J_c) - (J_{ea} + J_{ee}))/((J_{ae} + J_{aa}) - (J_{ea} + J_{ee}))$$

In this case the value for ΔE° is 1.22 ± 0.2 kcal/mol in acetone at 29°, not significantly different from the value calculated as above. Since no bands were observed for the *aa* conformation, the evidence favoring the latter treatment is negative only, and hence we prefer the former calculation.

Molecular mechanics calculations

Both 1,3-dichlorocyclohexane and 1,3-dichloro-5-methylcyclohexane were studied. We may examine the more simple compound first. Using the 1977 force field (MM2),[26] the diequatorial dichlorocyclohexane is calculated to be more stable than the diaxial by 2.39 kcal mol^{-1} (gas phase). The electrostatic contribution to the energy is higher in the diaxial, but accounts for only 0.47 kcal of the total energy difference. The van der Waals repulsion between the two chlorines is considerable, 0.51 kcal mol^{-1} at a distance of 3.37 Å, after the geometry is optimized and distorted so as to relieve this repulsion. There is an approximate increase of 1.0 kcal mol^{-1} in the bending energy in the diaxial compound, with the internal ring angle at the carbon carrying the chlorine opening to 115.5°. The 2.39 kcal mol^{-1} energy difference would be reduced with increasing dielectric constant of the solvent, approaching 1.92 kcal mol^{-1} as the latter became infinite.

Then, turning to the 1,3-dichloro-5-methylcyclohexane, we find that the effect of the methyl group is essentially additive. So the calculated energy difference between the diaxial dichloride and the diequatorial one in this compound is only 0.66 kcal mol^{-1} (gas phase), (*ca.* 2.39–1.70) or 0.21 kcal mol^{-1} (acetone) (*ca.* 1.92–1.70), in poor agreement with the value deduced experimentally (1.30 kcal mol^{-1}, acetone).

The electrostatics in molecules such as these is handled in the MM2 calculation by the dipole–dipole interaction method of Jeans, where the dielectric constant of the medium is taken to be 1.5 for the gas phase, and adjusted appropriately for different solvents.[27] This procedure is known to work reasonably well in most cases, but is a somewhat crude approximation.[29] Better procedures for treating the electrostatics have been developed,[22,28] and when used in conjunction with a solvation calculation which includes both the molecular dipole and quadrupole,[2] furnish more reliable results. When one of these schemes was applied in the present case,[22] it was found that the inductive effects greatly change the energies. In the case of the methyl derivative, the *ee* conformation was favored by 2.07 kcal mol^{-1} (gas phase). Solvation increased the amount of the *aa* conformation somewhat, although the effect was not very large. The conformational energy difference in acetone determined by the variable temperature method is a constant ($\Delta E_0^\circ = 1.3 \pm 0.2$ kcal mol^{-1} at −65°). On the other hand, the calculated values[22] of ΔE° for acetone vary with temperature, because the dielectric constant and consequently the solvation energy change with temperature. Therefore, in order to compare the calculated values (ΔE°) to the experimental one (ΔE_0°) the following relationship[2] was used:

$$\Delta E_0^\circ = \Delta E^\circ + t\frac{dH}{dT}$$

where H is solvation energy and T is the temperature. The term dH/dT was found (from the variation of dielectric constant with temperature) to have the value −0.00128 kcal mol^{-1} for acetone solution, and at the temperature used (−65°) TdH/dT had the value −0.27 kcal mol^{-1}. This gives a value for $(\Delta E^\circ + T(dH/dT)) = 1.67$ kcal mol^{-1}, compared with the experimental value of $\Delta E_0^\circ = 1.3 \pm 0.2$ kcal mol^{-1}. If the effect of the methyl group is additive as suggested above, then for *cis*-1,3-dichlorocyclohexane itself the diequatorial conformation would be preferred over the diaxial by $(1.7 + 1.3) = 3.0$ kcal mol^{-1} in acetone at room temperature, based on the low temperature experimental value.

EXPERIMENTAL

Gas-liquid chromatography was carried out on a Varian Aerograph Model 920 using the following columns (with Chromosorb P support): A, 10% FFAP, 2 m × 6 mm, glass; B, 10% Carbowax 20 M, 2 m × 6 mm, glass. Temperatures were 170° for diols and 120–130° for dichlorides, and flow rates of 60–100 ml min^{-1} of hydrogen were employed. The IR spectra were recorded on a Perkin–Elmer 337 spectrophotometer; NMR spectra were obtained on a Varian A-60A (60 MHz) spectrometer; the low temperature ^{1}H-NMR spectra were recorded on a JEOL PS/PFT 100 pulsed NMR spectrometer. Line positions were referenced to tetramethylsilane (TMS), calculated by the computer, and are accurate to the line-width described by one data point (0.12 Hz). The instrument was locked on the deuterium resonance of the solvent. Spectra were normally taken with a 500 Hz band width, with 8 K data points assigned to the FID. A 45° pulse of 20.4 μsec at a 9.0 sec^{-1} pulse repetition rate was generally used. ^{1}H-NMR spectra (low temperature) were recorded at the University of Georgia. The ^{13}C-NMR spectra were recorded in the Varian NMR Applications Laboratory, Zug, Switzerland on a Varian FT-80A spectrometer equipped with a Fourier transform accessory under the following conditions: spectral widths 4000 Hz and 2000 Hz and acquistion times 2.047s and 4s, respectively; pulse width 12 μs; solvent and lock $CDCl_3$. The mass spectra were recorded on a Varian MAT CH-5 high resolution spectrometer.

In the dipole moment measurements, the indices of refraction were measured on a Abbe, Carl Zeiss refractometer. The densities were recorded on a Anton Paar digitale dichtemesseinrichtung. For the dielectric constant measurements a WTW dipolmeter DM01 was used, with a measuring frequency of 2Mc/s. A.R. grades of *n*-hexane (Carlo Erba) and CCl_4 (E. Riedel) were used after being dried over molecular sieves.

Melting points (corrected) were measured on a Buchi apparatus (Schmelspunktbestimmungs-Apparat nach Dr. Tottoli).

The reactions were followed by tlc (Kieselgel $HF_{254+366}$, nach Stahl. Type 60, Merck) utilizing 50% H_2SO_4 as a visualization spray for location of compounds. The developing solvent mixture (for diols) was *n*-hexane: EtOAc = 6 : 4 and pure *n*-hexane for dichlorides.

Catalytic hydrogenation of orcinol monohydrate (*3,5-dihydroxytoluene*)

Orcinol monohydrate, 10 g, was dissolved in glacial acetic acid (200 ml) and was hydrogenated overnight with 5% Rh/Al_2O_3 (1 g) in a Parr shaker (73 psi). The solution was filtered and the solvent was evaporated. Distillation yielded 7.58 g (85%) of a mixture of 5-methyl-1,3-cyclohexenediols (97% pure by glc), b.p. 148–152° (25 mm), which was suitable for the next step. This material could be separated into two components, about 50% of each, by glc on a column A. The material which came off first was

5-methyl-*r*-1,*t*-3-cyclohexanediol (**2**): m.p. 145° (lit. 145–6°;[11] 147°.[12] This was followed by *c*-5-methyl-*r*-1,3-cyclohexanediol (**1**): m.p. 95° (lit. [12] 96°).

Hydrogenation of orcinol in glacial acetic acid with PtO_2 gave a distilled product mixture (32% yield), which analyzed on column B as consisting of 81% of **1** and 19% of **2**.

Hydrogenation with Raney nickel at 130°–160°/100–120 atm in ethanol/sodium ethoxide gave 14.6% **2**, crystallized from chloroform, m.p. 145°. From the filtrate additional crystals (**1** + **2**) were obtained, which could be separated on column B. Crystallization of the filtrate in ethyl acetate–benzene (1 : 1) yielded **3** m.p. 94°(lit.[12] 92°).

1,3-*Dichloro-5-methylcyclohexane*

A mixture of cyclohexanediols **2** and **1** (30 g, 0.23 mol) and pyridine (3 ml) was cooled in an ice-water bath and thionyl chloride (65.6 ml, 0.9 mol) was added dropwise. The mixture was allowed to stand overnight at room temperature, and then was gently refluxed for 2 hr at 50°. The reaction was followed by tlc and completion was based on the disappearance of the starting material from the tlc plates. The mixture was then cooled and water was added. The aqueous layer was extracted with ether, and the ethereal layer was separated, washed well with water and sodium bicarbonate solution, and dried over anhydrous sodium sulfate. The solvent was removed under vacuum on a rotary evaporator, and a dark yellow oil was obtained (28.2 g). A small sample of crude reaction product was analyzed by glc (column A) in order to determine its composition. The compound first eluted was the predominant product **8**, which according to the IR, NMR and mass spectra contained one chlorine atom and a double bond. The second and third components were 1,3-dichloro-5-methylcyclohexanes. The remaining crude oil was distilled under reduced pressure (84–100°/*ca.* 20 mm Hg) to yield 5.16 g (13.4%) of the mixed dichlorides **4** and **5**, which were further separated and purified by glc on column A. The material first eluted was the *r*-1,*t*-3-dichloro-5-methylcyclohexane **4**, 1.98 g (5.1%): $n_D^{20} = 1.4831$; dipole moment 2.2D (*n*-hexane), 2.27D (CCl_4). IR (film) 2980, 1470, 1275, 877, 780, 595 cm^{-1}. NMR (CCl_4) δ 0.98 (3H, d, J = 7 Hz, CH_3), δ 1.10–2.75 (7H, m), δ 4.0–4.65 (1H, m, H–C_1), and δ 4.4–4.5 (1H, m, H–C_3). MS *m/e* 166, 168, 170 (2%, M^+), 130, 132 (47%, M^+–HCl), 95 (100%, $C_7H_{11}^+$). Calc. for $C_7H_{12}Cl_2$: C, 50.32; H, 7.24; Cl, 42.48; Found: C, 50.29; H, 7.29; Cl, 42.89%. The second component eluted from the column was *r*-1,*c*-3-dichloro-*t*-5-methylcyclohexane-(**5**) 1.28 g (3.3%). $n_D^{20} = 1.4890$; dipole moment 2.48 D (CCl_4); IR (film) 2985, 1480, 1320, 837, 722 cm^{-1}. NMR (CCl_4) δ 1.02 (3H, d, J = 7 Hz, CH_3); δ 1.40–2.85 (7H, m), δ 4.02 (2H, m, J = 5 Hz, J = 11 Hz, H–C_1 and H–C_3). MS *m/e* 166, 168, 170 (9%, M^+), 130, 132 (7%, M^+–HCl), 95 (100%, $C_7H_{11}^+$). Calc. for $C_7H_{12}Cl_2$: C, 50.32, H, 7.24: Cl, 42.48; Found: 50.30; H, 7.37; Cl, 42.57%.

The reaction was also carried out with triphenylphosphine in carbon tetrachloride. Triphenylphosphine (60.44 g) dissolved in dry CCl_4 (120 ml) was added rapidly to 15 g of mixed diols **1** and **2**. The reaction was allowed to reflux for 1 hr and was monitored by tlc. After 1 hr an additional 15.11 g of triphenylphosphine in 30 ml of dry CCl_4 was added, and the mixture was then refluxed for 30 min. The products were separated from the reaction mixture by stream distillation, and were collected in a flask cooled in an ice–water bath. The organic layer was removed and dried over anwhydrous sodium sulfate. The solvent was evaporated in a rotary evaporator, yielding 10.7 g of residual oil. A small sample of this oil was analyzed by glc (column A) and showed three major components: **8** 4.41 g (29.4%), **4** and **5**. Distillation and purification by preparative glc, yielded 0.41 g (2.1%) of **4** and 0.89 g (4.6%) of **5**. Component **8** appears to be a mixture of isomeric compounds which contain one double bond and one chlorine atom. In MS the molecular ion is observed at *m/e* 130, 132 and the major fragments are at *m/e* 94 (M^+–Cl'), *m/e* 94 (M^+–HCl) and *m/e* 79 (*m/e* 94–'CH_3), confirmed by a metastable peak at *m/e* 66.4. IR (film) 3060, 2985, 1670, 1480, 1270, 700 cm^{-1}. The NMR spectrum suggest the existance of isomers which differ in the location of the double bond. NMR (CCl_4) mixture of **8-a**: δ 1.05 (3H, d, J = 7 Hz, CH_3); δ 1.40–2.90 (5H, m); δ 4.30 (1H, m, H–CCl); δ 5.57 (2H, m, –CH=CH–); and **8-b**: δ 1.02 (3H, d, J = 7 Hz, CH_3); δ 1.40–2.90 (5H, m); δ 4.58 (1H, m, H–CCl); δ 5.79 (2H, m, –CH=CH–).

The structures of the products **4** and **5** were established by comparison with the samples previously described.

Reaction of 5-*methyl*-1,3-*cyclohexanediol with* 36% *HCl*

A mixture of cyclohexanediols **1** and **2** (1.1 g, 0.008 mol) and 36% HCl (3 ml) was sealed in a Carius tube and allowed to stand 7 hr at 100–110°. The mixture was then cooled, water was added, and the aqueous layer was extracted with ether several times. The ethereal layer was separated, washed well with water and saturated sodium bicarbonate solution, and dried over anhydrous sodium sulfate. The solvent was removed yielding 1.18 g of a crude yellow oil. According to the glc analysis on column A, a mixture of products was obtained with the major component *r*-1,*t*-3-dichloro-1-methylcyclohexane **7**: IR (film): 2975, 1470, 1230, 867, 792, 750, 570 cm^{-1}. NMR (CCl_4): δ 1.63 (3H, s, CH_3), δ 1.23–2.70 (8H, m), δ 3.90–4.47 (1H, m, H–C_3). MS *m/e* 166, 168, 170 (0%, M^+), 130, 132 (3%, M^+–HCl), 95 (100%, $C_7H_{11}^+$).

The analysis of **7** differs from the calculated values, probably because of the decomposition. For instance, glc at 120° (column A) indicated the partial decomposition of this compound.

When the mixture of diols **1** and **2** was heated in Carius tube with HCl (36%) and anhydrous calcium chloride, the amount of **7** was increased.

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