

both isomers are detected when R is ethyl or isopropyl. From the ultraviolet spectra, *e.g.*, decrease of λ_{\max} from 275 (R = CH₃, CH₂CH₃) to 250 m μ (R = isopropyl), it is deduced that when R is isopropyl the interactions between phenyl and isopropyl in isomer XXII are sufficiently large to cause loss of overlap between the phenyl and the NNO groups. The 224 m μ band, when R is isopropyl, could conceivably be the absorption of isomer XXIII.

Experimental

Amines used in the preparation of nitrosamines were commercially available compounds. Methyl-*t*-butylamine and ethyl-

benzylamine were prepared by lithium aluminum hydride reduction¹¹ of *t*-butylformamide and *N*-benzylacetamide.

Nitrosamines were prepared from the reaction of the corresponding amines with nitrous acid.¹¹

N.m.r. spectra were determined at 60 Mc. on a Model A-60 spectrometer (Varian Associates, Palo Alto, Calif.), at a temperature of about 36°. Undegassed solutions were used with tetramethylsilane as internal reference.

Ultraviolet spectra were taken with a Cary 14 recording spectrophotometer.

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Conformational Analysis. II.

Use of the Chemical Shift of the Hydroxyl Proton in Conformational Analysis

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Dilution studies have been carried out to determine the chemical shift of the monomeric hydroxyl proton in *cis*-4-*t*-butylcyclohexanol and *trans*-4-*t*-butylcyclohexanol in carbon tetrachloride. The hydroxyl proton in the axial position occurs at higher field than the hydroxyl proton in the equatorial position. The conformational preference of the monomeric hydroxyl group in cyclohexanol is 0.75 kcal./mole. The chemical shifts of the hydroxyl proton in pyridine and dimethyl sulfoxide are examined. These solvents do not significantly affect the conformational preference of the hydroxyl group.

Introduction

The conformational preference of the hydroxyl group in cyclohexanol has been determined by kinetic,^{1,2} equilibrium,^{3,4} infrared,^{5,6} and n.m.r.⁷⁻⁹ methods. The n.m.r. methods are the most direct and powerful available at this time. Eliel⁷ utilized the chemical shift of the α -hydrogen in cyclohexanol and established an approximate value of 0.6 kcal./mole for the conformational preference of the hydroxyl group. However, the signal of the α -hydrogen is broad and unresolved and, in order to improve the accuracy of the method, selective deuteration has been employed.^{8,9}

Recently the conformational preference of the ethynyl group was determined indirectly from the conformation of 1-ethylcyclohexanol.¹⁰ It was shown that the chemical shift of the hydroxyl proton is linearly related to concentration in the range of 0.002 to 0.02 mole fraction of alcohol in carbon tetrachloride. The conformational preference of the ethynyl group was found to be 0.60 kcal./mole smaller than that of the hydroxyl group. Winstein's⁸ value of 0.78 kcal./mole for the conformational preference of hydroxyl group was used in evaluating the conformational preference of the ethynyl group. Winstein's value was determined in a 20% solution in carbon tetrachloride. The hydroxyl group is strongly associated under these conditions and it is conceivable that the steric size of the hydroxyl group is a function of the degree of as-

sociation. Therefore it was decided to investigate the hydroxyl group under conditions where hydrogen bonding is minimal. As a result of this investigation, the effect of intermolecular hydrogen bonding and association with solvent should be directly available.

Results

In the previous paper of this series,¹⁰ it was shown that the chemical shift of the hydroxyl proton is linearly related to concentration at low mole fractions. The chemical shift of the monomeric hydroxyl proton can be obtained by extrapolation to infinite dilution.

The chemical shifts of the hydroxyl protons of *cis*-4-*t*-butylcyclohexanol and *trans*-4-*t*-butylcyclohexanol are derivable from the data given in Table I. Figure 1 shows the dependence of the chemical shift as a function of the mole fraction of compound in carbon tetrachloride containing 0.001 mole fraction of tetramethylsilane as the internal standard. The extrapolated chemical shifts of the axial and equatorial hydroxyl protons expressed in c.p.s. downfield from tetramethylsilane are 25.7 and 46.4, respectively. By comparison with previous work,¹⁰ the ethynyl group deshields the hydroxyl proton by approximately 46 c.p.s.

The data for the chemical shifts of the hydroxyl group in cyclohexanol are given in Table I and are illustrated in Fig. 1. The chemical shift at infinite dilution is 41.6 c.p.s. The equilibrium constant for the axial equatorial conversion is 3.3 ± 0.2 at 40°. This equilibrium constant corresponds to a free-energy change of 0.75 kcal./mole at 40°.

The chemical shift of the hydroxyl proton is independent of concentration in either pyridine or dimethyl sulfoxide in the concentration range used for the studies in carbon tetrachloride. Both pyridine and dimethyl sulfoxide shift the hydroxyl proton resonance signal to low field owing to hydrogen bonding. The chemical

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TABLE I
THE CHEMICAL SHIFT OF THE HYDROXYL PROTON IN CARBON TETRACHLORIDE

Compound	Mole fraction	Chemical shift ^{a,b}
<i>trans</i> -4- <i>t</i> -Butylcyclohexanol	0.00398	59.5
	.00572	65.4
	.00710	70.5
	.00842	72.8
	.00968	77.6
	.01103	82.2
	.01215	85.9
	.03210	88.8
	.01490	94.0
	<i>cis</i> -4- <i>t</i> -Butylcyclohexanol	.00210
.00401		36.2
.00593		40.4
.01300		58.5
.01451		61.9
.01639		66.7
.01319		83.2
Cyclohexanol	.00250	49.7
	.00448	55.8
	.00627	60.7
	.00902	70.1
	.01102	76.7
	.01319	83.2

^a C.p.s. downfield from tetramethylsilane as internal standard (0.001 mole fraction) in carbon tetrachloride. ^b At 40°.

shifts of each compound at 0.01 mole fraction in the two solvents are given in Table II. The equilibrium constant for the axial-equatorial conversion is 3.7 ± 0.2 in both solvents. The free-energy change at 40° is 0.80 kcal./mole in both pyridine and dimethyl sulfoxide.

TABLE II
THE CHEMICAL SHIFT OF THE COMPLEXED HYDROXYL PROTON

Compound	Solvent	Chemical shift ^{a,b}
Cyclohexanol	Dimethyl sulfoxide	262.7
<i>trans</i> -4- <i>t</i> -Butyl-	Dimethyl sulfoxide	267.1
<i>cis</i> -4- <i>t</i> -Butyl-	Dimethyl sulfoxide	246.6
Cyclohexanol	Pyridine	324.0
<i>trans</i> -4- <i>t</i> -Butyl-	Pyridine	328.5
<i>cis</i> -4- <i>t</i> -Butyl-	Pyridine	307.7

^a C.p.s. downfield from tetramethylsilane as internal standard (0.001 mole fraction). ^b At 40°.

It should be noted that the signals for all compounds investigated in dimethyl sulfoxide are doublets and appear as the low-field half of an AB system. Chapman¹¹ has recently reported this phenomenon. The values for the chemical shifts of the compounds investigated in this paper are in excellent agreement with those of Chapman. The coupling constants between the α -hydrogen and the hydroxyl hydrogen are 3.2, 4.2, and 4.3 c.p.s. for *cis*-4-*t*-butylcyclohexanol, cyclohexanol, and *trans*-4-*t*-butylcyclohexanol, respectively.

Discussion

The use of the chemical shift of the hydroxyl proton extends the utility of n.m.r. techniques in conformational analysis. The conformational free-energy preference of the hydroxyl group has been determined by a simple direct approach without the use of selective deuteration.

The determination of the conformational preference of the monomeric hydroxyl group establishes the

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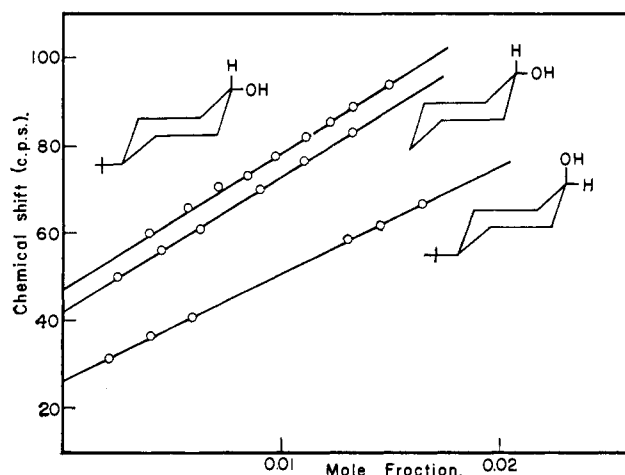


Fig. 1.—Chemical shift dependence of hydroxyl proton with concentration at 40°.

conformational preference of the ethynyl group which was previously estimated using an assumed value for the hydroxyl group.

Intermolecular hydrogen bonding does not affect the apparent steric size of the hydroxyl group. Winstein's value of 0.78 kcal./mole is in excellent agreement with this work.

That the conformational preference of the hydroxyl group is essentially independent of association with pyridine was not unexpected. Pyridine must be associated at the hydrogen atom which is β to the cyclohexane ring. However, the association with dimethyl sulfoxide could conceivably involve association at both the oxygen and hydrogen of the hydroxyl group. Therefore it was not immediately obvious that dimethyl sulfoxide would not affect the conformational preference of the hydroxyl group. Ritchie¹² has found that dimethyl sulfoxide forms 1:1 complexes with nitriles and complexation significantly affects the base-catalyzed equilibration of *cis*- and *trans*-4-*t*-butylcyclohexylcarbonitrile. It has been suggested by Ritchie that complexing with the *cis* isomer can only occur from the "front side" of the nitrile, whereas complex formation can occur at "either side" in the *trans* isomer. If it is assumed that the hydroxyl-dimethyl sulfoxide complex is geometrically similar to the nitrile-dimethyl sulfoxide complex, then the methyl groups of the solvent are directed toward the ring in the *cis* isomer as shown in Fig. 2. Since complexing is probably not restricted from the ring side owing to the angular nature of the hydroxyl group, the difference between Ritchie's work and these observations can be reconciled. That the hydroxyl hydrogen and the α -hydrogen are cisoid is supported by the observed coupling constant of 3.2 c.p.s. in the *cis* isomer. In the *trans* isomer, the hydroxyl group is free to assume a transoid configuration and a coupling constant of 4.3 c.p.s. is observed.

A detailed study of the ethanol hydroxyl dilution shift has been carried out by Becker, Liddel, and Shoolery.¹³ They observed a linear dependence of the chemical shift with concentration below 0.015 mole fraction. The linearity observed with the cyclohexanol system is in agreement with their work.

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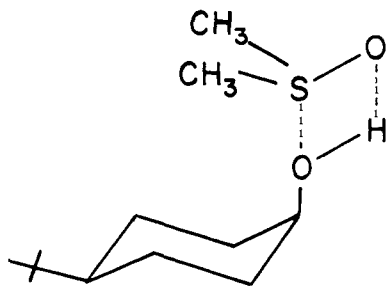


Fig. 2.—Dimethyl sulfoxide with *cis*-4-*t*-butylcyclohexanol.

It is interesting to note that not only is the chemical shift of the hydroxyl proton a function of stereochemistry, but the slope of the line relating the chemical shift with concentration in carbon tetrachloride is also. As was previously pointed out,¹⁰ one would expect the hydroxyl group in the axial position to be less hydrogen bonded than in the equatorial position. In the axial position the hydroxyl group can probably be bonded best with the hydrogen directly away from the plane of the ring. The slopes for *cis*-4-*t*-butylcyclohexanol and *trans*-4-*t*-butylcyclohexanol are 2510 and 3160 c.p.s./ N_{ROH} respectively. The slopes for

1-ethynyl-*cis*-4-*t*-butylcyclohexanol and 1-ethynyl-*trans*-4-*t*-butylcyclohexanol are 690 and 1060 c.p.s./ N_{ROH} respectively. This phenomenon is currently being investigated for the purpose of determining whether the slope of the concentration-chemical shift relationship can be useful in confirming and assigning stereochemistry.

Experimental

Carbon tetrachloride was distilled at atmospheric pressure in a dry system under nitrogen. Pyridine and dimethyl sulfoxide were distilled from calcium hydride under reduced pressure. The dimethyl sulfoxide was stored over Linde Molecular Sieve 4A. Tetramethylsilane was added to all solvents to produce solutions that were approximately 0.001 mole fraction in internal standard.

All glassware was dried and placed in a vacuum desiccator. All manipulations were carried out under a nitrogen atmosphere to eliminate uptake of atmospheric moisture. Solutions were prepared in 2- and 5-ml. volumetric flasks and the weights of compound and solvent were determined by difference.

Spectra were obtained with a Varian Associates A-60 spectrometer. The probe temperature was 40°. The chemical shifts were determined to 0.2 c.p.s. The position of the *t*-butyl hydrogen and solvent signals where applicable were used as additional internal references.

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Equilibrium Rearrangement of Perchlorocarbon Compounds

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By heating any perchlorocarbon compound or mixture of compounds having an over-all mole ratio of chlorine to carbon between 1 and 4, an equilibrium is reached in a closed condensed fluid system between hexachlorobenzene, carbon tetrachloride, and smaller amounts of hexachloroethane; no carbonization was observed under any conditions investigated. The equilibrium constant is reported for the temperature in the 400–460° range and data on the kinetics of decomposition of octachloropropane are discussed in terms of a probable free-radical mechanism. The aromatization reaction which gives rise to hexachlorobenzene is shown to be reversible.

In the past, high-temperature reactions of perchlorocarbon compounds have been studied by an open system or flow techniques.^{2,3} Some short-time studies have also been made under pressure.^{4,5} However, the present work is believed to be the first investigation of the interconversion of these compounds under conditions where chemical equilibration is demonstrable. The equilibrium involves both aromatic and aliphatic carbon structures—with the proportions of the various compounds present in equilibrium depending only on the ratio of chlorine to carbon in the starting mixture. In those studies^{2,6} in which activated carbon was used as a catalyst, it is not clear whether carbon is formed during the reaction. Therefore, no such catalyst was employed in the studies reported below.

Experimental Section

Reagents.—The materials used were the purest grade commercially available products and were further purified when gas

chromatography indicated more than 1% of impurities. The carbon tetrachloride was Baker and Adamson reagent grade material, and the tetrachloroethylene (redistilled), hexachlorobenzene, and hexachloroethane were Eastman White Label products. The octachloropropane from Columbia Organic Chemicals, Columbia, S. C., was found to have 11.5% C and 88.5% Cl, with no H or O (theory: 11.3% C, 88.7% Cl). The hexachlorobutadiene, hexachloropropene, and hexachlorocyclopentadiene, obtained from K and K laboratories, Jamaica 33, N. Y., exhibited the physical constants reported in the literature.

Equilibration.—The reactions were conducted in sealed Pyrex tubes (o.d. 6 mm., i.d. 4 mm.) which were placed inside steel guard-tubes during heating. [The 1-mm. glass wall thickness was found to withstand adequately the pressures (up to ca. 200 atm.) developed.] In all cases, the tubes were sealed so as to have the liquid nearly filling their entire volume (ca. 95%) at the reaction temperature so that, for practical purposes, only a single phase was considered to be present. Heating was carried out for the desired length of time in one of three furnaces held at 345 ± 15°, 405 ± 4°, and 455 ± 4°. Occasional visual observation of the heated tubes indicated that those having high values of $R \equiv \text{the Cl/C over-all mole ratio}$ were supercritical. In order to fix the zero time in the kinetic studies of the decomposition of octachloropropane and of hexachloroethane, the sealed glass tubes were inserted in the steel guard-tubes which had been preheated to the reaction temperature. At the end of a given run, the tube was quenched in cold water. For these two rate studies, the furnace temperatures were maintained at 350 ± 3° and 400 ± 3°, respectively.

Analysis.—A Microtek GC-2500 dual column gas chromatograph was used for analysis, employing a thermal-conductivity detector and a variable-temperature programmer. The 5-ft. long column was packed with a sorbent consisting of 10% Dow-

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