solution through the vapor phase chromatograph, the 13.5-min. peak had disappeared, and the ratio of the 8.8-min. peak to the 14.2-min. peak was 3.45:1.

The 13.5-min. peak was collected by vapor phase chromatography, and its n.m.r. and infrared spectra were obtained. This sample became brown during the time required to collect a sufficient sample for the spectra. When the n.m.r. sample was rechromatographed, the presence of a small amount of methyl 5-nonyl ether and approximately equivalent amounts of the 13.5-min. component and 6-butyl-5-decanone was indicated.

Reaction of Dichloromethyl Methyl Ether and *n*-Butyllithium in the Presence of 2-Methylpropene.—In the same manner as in the reaction of dichloromethyl methyl ether and *n*-butyllithium in the presence of cyclohexene, 11.5 g. (0.1 mole) of dichloromethyl methyl ether, 94 g. of 2-methylpropene, and 65 ml. (0.1 mole) of 1.5 *N* *n*-butyllithium in hexane were added together to yield, according to the integrated vapor phase chromatographic analysis, 2.9 g. (24%) of methyl 5-nonyl ether and 0.3 g. (3%) of 6-butyl-5-decanone.

Reaction of Dichloromethyl Methyl Ether and Methyllithium in the Presence of 2-Methylpropene.—To 20.7 g. (0.18 mole) of dichloromethyl methyl ether in 90 g. of 2-methylpropene maintained at −10 to −15° was added with rapid stirring 200 ml. (0.18 mole) of 0.905 *N* methyllithium in ether over a period of 1 hr. Cooling was continued for an additional 2 hr. after which time the reaction mixture was allowed to warm to room temperature. Water was added to the mixture, the ether layer was separated, and the aqueous layer was extracted twice more with ether. The ethereal solutions were combined and dried over anhydrous sodium sulfate. The ether was distilled from the solution, leaving a residue weighing 16.0 g., which on vapor phase chromatography using a 6 ft. × 0.25 in. γ,γ-nitromethylpimelonitrile-on-firebrick column was shown to contain 8.5 g. (53.8% yield) of 2,2-dimethylmethoxycyclopropane. The n.m.r. spectrum of a sample collected from the vapor phase chromatograph showed peaks at τ 6.74 (singlet) (3), 7.21 (multiplet) (1), 8.90 (singlet) (3), 9.04 (singlet) (3), and 9.73 (multiplet) (2). This agrees with the spectrum published.[3]

Dichlorodiphenoxymethane.—The procedure of Gross and coworkers[8] was followed for the preparation of this compound, b.p. 164–167° (6 mm.), 49% yield [lit.[8] b.p. 183–185° (12 mm.), 63% yield].

Reaction of Dichlorodiphenoxymethane and *n*-Butyllithium in the Presence of Cyclohexene.—To a solution of 24.6 g. (0.3 mole) of cyclohexene and 33.0 g. (0.089 mole) of dichlorodiphenoxymethane in 200 ml. of dry ether cooled to −70°, 100 ml. (0.13 mole) of 1.28 *N* *n*-butyllithium in hexane was added dropwise over a period of 2 hr. Stirring of the mixture was continued overnight as the mixture was allowed to come to room temperature. The reaction mixture was filtered, the precipitate was dissolved in water and extracted with chloroform, and the chloroform extracts were dried over calcium chloride. The chloroform was removed from the solution under reduced pressure yielding 3.7 g. of tetraphenoxyethylene, m.p. 163–167°. Recrystallization from chloroform gave colorless crystals, m.p. 166.5–168° (lit.[16] m.p. 168°), which were further identified by their infrared and n.m.r. (multiplet centered at τ 2.98) spectra.

Distillation of the filtrate gave only a small amount of phenol after removal of the solvents. The residue from the distillation yielded an additional 0.40 g. of tetraphenoxyethylene, giving a total of 4.1 g. (23% yield).

Reaction of Dichlorodiphenoxymethane and Methyllithium in the Presence of Cyclohexene.—A solution of 16.4 g. (0.2 mole) of cyclohexene and 13.5 g. (0.05 mole) of dichlorodiphenoxymethane in 300 ml. of anhydrous ether under nitrogen was cooled to −72°. To this was added dropwise over a period of 1 hr. with rapid stirring, 0.104 mole of methyllithium [prepared from 2.3 g. (0.33 g.-atom) of lithium in 50 ml. of ether and 21.33 g. (0.15 mole) of methyl iodide]. While the stirring was continued, the reaction mixture was allowed to warm. During this period the reaction mixture began to turn red and was maintained at −40 to −35° for 30 min. The dark color was found to be due to iodine and was removed by washing the reaction mixture with aqueous sodium thiosulfate. This procedure was repeated several times over a period of 2 days. The ethereal solution was dried over sodium sulfate and the ether then was distilled off, leaving 7.9 g. of crystalline material which was recrystallized from ethanol to give 6.98 g. (88%) of tetraphenoxyethylene, m.p. 168–169°.

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Cycloheptanol. Steric Influence of the 4-*t*-Butyl Group

DONALD D. ROBERTS

Department of Chemistry, Louisiana Polytechnic Institute, Ruston, Louisiana 71271

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The *t*-butyl group, by acting as a remote but compelling control, has been used extensively to confer conformational stability to a 1-substituent on a cyclopentane,[1] cyclohexane,[2-4] and cyclooctane[5] ring. The ability of a *t*-butyl group to impart analogous steric control on a 1-substituted cycloheptane ring remains to be studied.

Based on the computed *A* value,[2] the equatorial position of the *t*-butyl group on a cyclohexane ring is favored over the axial position by 5.4–5.8 kcal./mole, a value sufficiently large to compel the *t*-butyl group to be equatorial. A similar equatorial preference for the *t*-butyl group would be expected on the cycloheptane ring in a pseudo-chair form; however, if the seven-membered ring is predominantly in the twist-chair form,[6] it is to be expected that slight conformational preference would be exerted by a *t*-butyl group bonded to an axis carbon.

The purpose of this paper is to measure the degree of conformational stability imparted by a 4-*t*-butyl group on cycloheptanol. To this end, gas chromatographic (including capillary column g.c.), n.m.r., and kinetic methods have been applied.

Results

4-*t*-Butylcycloheptanone (2) was prepared by the diazomethane ring expansion of 4-*t*-butylcyclohexanone (1). The reduction of ketones 1 and 2 with three reducing reagents is summarized in Table I. The 4-*t*-butylcyclohexanol (3) compositions were determined by gas chromatography at 160° using three 5-ft. columns packed with (1) 40–60-mesh Tide soap, (2) 20 wt. % 1,2,3-tris(2-cyanoethoxy)propane on 30–60-mesh Chromosorb, and (3) 20 wt. % diethylene glycol succinate on 30–60-mesh Chromosorb. Excellent separation was obtained for all epimeric mixtures of 4-*t*-butylcyclohexanol.

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TABLE I

SUMMARY OF 4-*t*-BUTYLCYCLOALKANONE REDUCTIONS

Ketone	Time, min.	Conversion,[a] %	No. of runs	No. of alcohols identified[b]	% *trans*
		Reductions with $LiAlH_4$			
1	120[c]	100	2	2	90
2	10	99	1	1	
	180	100	1	1	
	1080	100	3	1	
		Reductions with PtO_2–H_2			
1	15	100	3	2	10
	15[d]	100	1	2	75
2	15	100	4	1	
	15[d]	100	1	1	
	20	100	3	1	
	60	100	2	1	
		Reductions with $NaBH_4$			
1	180	100	1	2	85
2	180	100	1	1	

[a] Based on conversion of ketone to alcohol. [b] Identification by gas chromatography and n.m.r. spectroscopy; *cf.* text for details. [c] Taken from data of E. L. Eliel and M. N. Rerick, *J. Am. Chem. Soc.*, **82**, 1367 (1960). [d] Reactions were carried out in the absence of concentrated hydrochloric acid.

Reduction of ketone **1** with lithium aluminum hydride, sodium borohydride, and hydrogen over platinum oxide (in the absence of concentrated hydrochloric acid) leads to the expected preponderance of *trans*-4-*t*-butylcyclohexanol. Reduction with hydrogen over platinum oxide (in the presence of concentrated hydrochloric acid) leads to a reversal of the 4-*t*-butylcyclohexanol isomer composition in accord with the von Auwers–Skita hydrogenation rule.[7]

Analysis of the 4-*t*-butylcycloheptanol (**4**) samples by capillary column gas chromatography at 175° with (1) a 100-ft. silicon oil column and (2) a 100-ft. polypropylene glycol column gave a single broad peak. Conversion of aliquots from the alcohol samples to their trimethylsilyl derivative[8] gave a single sharp peak. Mixtures of the trimethylsilyl derivatives of the various 4-*t*-butylcycloheptanol samples yielded chromatograms with only one sharply resolved peak.

The n.m.r. spectral data for cycloheptanol and 4-*t*-butylcycloheptanol are given in Table II. The assignment of the sharp singlet at τ 6.80 (in carbon tetrachloride) and the poorly resolved doublet at τ 6.65 (in DMSO) to the hydroxyl proton was made on the basis of a concentration-dependency study in carbon tetrachloride.

TABLE II

N.M.R. SPECTRAL PARAMETERS[a]

Compd.	Solvent[b]	Proton α-H	Chemical shift, -OH
Cycloheptanol	CCl_4	6.30	6.70
4-*t*-Butylcycloheptanol[c]	CCl_4	6.30	6.80
4-*t*-Butylcycloheptanol[d]	CCl_4	6.30	6.80
4-*t*-Butylcycloheptanol[e]	CCl_4	6.30	6.80
Cycloheptanol	DMSO	5.73	6.65
4-*t*-Butylcycloheptanol[c]	DMSO	5.73	6.65
4-*t*-Butylcycloheptanol[d]	DMSO	5.73	6.65
4-*t*-Butylcycloheptanol[e]	DMSO	5.73	6.65

[a] Obtained with a Varian HA-60 n.m.r. spectrometer. [b] All samples approximately 0.1 mole fraction of alcohol. [c] Prepared *via* the $LiAlH_4$ reduction of the ketone. [d] Prepared *via* the $NaBH_4$ reduction of the ketone. [e] Prepared by the reduction of the ketone with hydrogen over PtO_2 in the presence of hydrochloric acid.

Since the n.m.r. spectrum of a mobile molecule such as cycloheptanol reflects the average positions of the pertinent protons in the pseudo-rotation itinerary,[9,10] the near equivalency of the chemical shift values[11] for all the samples suggests the presence of similar mobility in the 4-*t*-butylcycloheptanol molecule. More specifically, the n.m.r. data coupled with the capillary column g.c. data suggest a lack of any significant influence by the 4-*t*-butyl group on the conformational preference of the 1-hydroxyl group.

Additional support is given this thesis by a study of saponification rates of the acid phthalates reported in Table III. All the measured reactions followed strictly second-order kinetic law up to 90% conversion. It is to be expected that, if the average position of the acid phthalate group in both compounds is similar, near identical partitioning of the activation parameters would occur. The activation enthalpy and entropy values given in Table III are nearly equivalent and, therefore, suggest that the fluctuations in position of the phthalate group are not significantly restricted by the *t*-butyl group.

TABLE III

RATES OF SAPONIFICATION OF ACID PHTHALATES IN AQUEOUS SODIUM HYDROXIDE

Acid phthalate	Temp., °C.	Phthalate, $M \times 10^2$	NaOH, $M \times 10^2$	$10^4 k_2$, l. mole^{-1} sec.$^{-1}$
Cycloheptyl[a]	50.0	2.70	7.00	7.2 ± 0.1[b]
	50.0	3.00	6.60	7.3 ± 0.05
	60.0	3.00	6.52	13.7 ± 0.01
	70.0	3.45	6.45	25.8 ± 0.2
	70.0	3.00	6.50	25.9 ± 0.1
4-*t*-Butylcycloheptyl[c]	50.0[d]	3.00	6.40	4.2 ± 0.05
	50.0[e]	2.55	6.85	4.1 ± 0.05
	50.0[e]	2.90	6.50	4.2 ± 0.08
	60.0[d]	2.95	6.43	7.8 ± 0.08
	60.0[e]	2.95	6.43	7.8 ± 0.08
	70.0[d]	3.00	6.45	15.5 ± 0.1
	70.0[e]	3.40	6.40	15.4 ± 0.1

[a] $\Delta H^* = 13.3 \pm 0.08$ kcal./mole, $\Delta S^* = -23$ e.u. [b] One standard deviation unit from the mean. [c] $\Delta H^* = 13.7 \pm 0.12$ kcal./mole, $\Delta S^* = -32$ e.u. [d] The alcohol was prepared *via* $LiAlH_4$ reduction of the ketone. [e] Alcohol prepared by reduction of the ketone with hydrogen over PtO_2 in the presence of hydrochloric acid.

A possible rationale for the observed facts is afforded by an examination of the framework molecular-orbital models of both *cis*- and *trans*-4-*t*-butylcycloheptanol in the twist-chair form. If the 4-*t*-butyl group is placed on the axis carbon,[12] then the ring can easily be flipped to convert an axial OH to an equatorial OH without

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(10) J. B. Hendrickson, *J. Am. Chem. Soc.*, **84**, 3355 (1962).

(11) The α-hydrogen was a broad band in carbon tetrachloride; however, in DMSO a triplet (poorly resolved in most spectra) was obtained which is in keeping with the molecular models for the twist-chair form and the Karplus equation: see M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

(12) The possibility exists that the compounds may partition themselves among additional conformations *via* pseudo-rotation (*cf.* ref. 10); however, the apparent lack of hydroxyl group conformational preference is best accommodated by placing the 4-*t*-butyl group on the axis carbon.

introducing a significant change in the group bonded to the axis carbon. Thus, the conformational preference of the hydroxyl group on the 4-*t*-butyl-substituted ring should be similar to the hydroxyl group on the nonsubstituted cycloheptanol, which would account for the physically indistinguishable *cis* and *trans* isomers.

Experimental Section[13]

4-*t*-Butylcyclohexanone (1) was prepared in 82% yield by chromic acid oxidation of commercial 4-*t*-butylcyclohexanol, m.p. 48–49°, lit.[14] m.p. 49–50°.

4-*t*-Butylcycloheptanone (2).—A mixture of 4-*t*-butylcyclohexanone (72 g., 0.5 mole) and *p*-tolylsulfonylmethylnitrosamide (125 g., 0.58 mole) in 160 ml. of 89 vol. % aqueous ethanol was cooled to 0°, and a solution of 15 g. of potassium hydroxide in 50 ml. of 50% aqueous ethanol was added dropwise with stirring over 2 hr. The addition rate was such as to maintain the temperature at 15–20°. Work-up according to the procedure of deBoer and Backer[15] gave the the ketone in 49% yield, b.p. 68° (0.2 mm.).

Anal. Calcd. for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.58; H, 11.90.

4-*t*-Butylcycloheptanol (4). **A. By Reduction of 4-*t*-Butylcycloheptanone with Lithium Aluminum Hydride.**—A solution of 4-*t*-butylcycloheptanone (11.0 g., 65 moles) in 20 ml. of anhydrous ether was added dropwise over a 30-min. period[16] to a stirred suspension of lithium aluminum hydride (1.2 g., 30 mmoles) in 100 ml. of anhydrous ether cooled by means of an ice–water bath. After stirring an additional 18 hr. (3 hr. for one run), the excess hydride and alcoholate were destroyed with 20 ml. of water, and the precipitate formed was dissolved in 80 ml. of 10% aqueous sulfuric acid. Extraction with ether, drying over anhydrous sodium sulfate and distillation gave the alcohol in 85% yield, b.p. 72° (0.2 mm.), $n^{25}D$ 1.4751.

Anal. Calcd. for $C_{11}H_{20}O$: C, 77.58; H, 13.03. Found: C, 77.52; H, 12.98.

B. By Reduction of 4-*t*-Butylcycloheptanone with Hydrogen over Platinum Oxide.—A solution of 4-*t*-butylcycloheptanone (6.6 g., 40 mmoles) in 50 ml. of glacial acetic acid containing 6 drops of concentrated hydrochloric acid was shaken with 400 mg. of platinum oxide (Englehard Industries, 82.3%) under 30 p.s.i. of initial hydrogen pressure for 15 min. The uptake of hydrogen was in good agreement with the theoretical amount. After removal of the spent catalyst, the reaction mixture was diluted with 5 vol. of water and continuously extracted with ether for 24 hr. The ether phase was separated, neutralized with aqueous sodium bicarbonate, and dried over anhydrous sodium sulfate. Distillation gave the alcohol in 95% yield. Identity with the alcohol obtained by procedure A was established by n.m.r. spectroscopy and capillary column gas chromatography.

C. By Reduction of 4-*t*-Butylcycloheptanone with Sodium Borohydride.—A mixture of sodium borohydride (0.35 g., 9 mmoles) in 8 ml. of water was added dropwise over a 10-min. period to a stirred solution of 4-*t*-butylcycloheptanone (4.0 g., 24 mmoles) in 20 ml. of methanol. After stirring at reflux temperature for 1 hr. and at room temperature for 2.5 hr., the salt was decomposed by the addition of 80 ml. of 10% sodium hydroxide. Extraction with ether, washing with saline solution, drying over anhydrous sodium sulfate, and distillation gave the alcohol in 92% yield. Identity with the alcohol obtained by procedure A was established by n.m.r. spectroscopy and capillary column gas chromatography.

Cycloheptanol (5).—Reduction of cycloheptanone with lithium aluminum hydride gave the alcohol in 85% yield: b.p. 42° (0.4 mm.), $n^{25}D$ 1.4750; lit.[17] b.p. 88° (18 mm.), $n^{20}D$ 1.4747.

Cycloheptyl acid Phthalate (6) was prepared by the conventional procedure yielding white needles, m.p. 100–101°, after two recrystallizations from petroleum ether (b.p. 30–60°), lit.[18] m.p. 100–102°.

4-*t*-Butylcycloheptyl Acid Phthalate (7).—In a typical preparation, a solution of 2.5 g. of 4-*t*-butylcycloheptanol and 2.3 g. of phthalic anhydride in 10 ml. of dry pyridine was kept at 100° for 20 hr. Working up in the usual way gave an oil which was crystallized from petroleum ether. The first crop, m.p. 79–81°, yielded 2.7 g. of material. After two additional crystallizations, the melting point was 83–85°.

Anal. Calcd. for $C_{19}H_{26}O_4$: C, 71.67; H, 8.23. Found: C, 71.44; H, 8.28.

Kinetic Measurements on Saponification of Acid Phthalates.—The measurements were carried out with samples of cycloheptyl (6) and 4-*t*-butylcycloheptyl (7) acid phthalates purified by four recrystallizations from petroleum ether.

Standard aqueous sodium hydroxide was prepared using conductivity water. Frequent restandardization failed to reveal any significant variation in normality.

The acid phthalate was weighed out in a volumetric flask, brought up to volume with excess standard aqueous sodium hydroxide, and placed in a constant-temperature bath (accurate to ±0.1°). Aliquots were removed periodically, the reaction was quenched by chilling in ice–water, and the remaining sodium hydroxide was titrated with 0.05 *N* standard potassium acid phthalate to a cresol red end point.

The rate constants were calculated using the integrated form of equation for a second-order reaction.

The thermodynamic activation functions were obtained by IBM 1620 computer regression analysis of $\ln k/T$ *vs.* $1/T$.

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Free-Radical Reactions of Diethylketene Acetal

EARL S. HUYSER, RICHARD M. KELLOGG,[1] AND DOROTHY T. WANG[2]

Department of Chemistry, University of Kansas, Lawrence, Kansas

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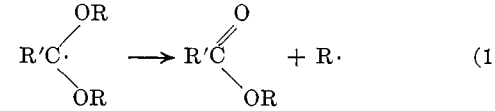
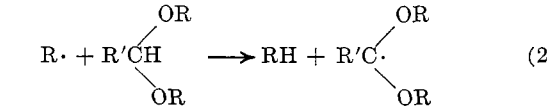
The major reaction products of the peroxide-induced reactions of acetals are alkanes and esters. A free-radical chain sequence involving the β elimination of an alkyl radical from an α,α-dialkoxyalkyl radical (reaction 1) which is produced by abstraction of the α-hydrogen from the parent acetal by the eliminated alkyl radical (reaction 2) has been proposed as the mechanism for these reactions.[3] Addition of a free



(1)



(2)

radical to a dialkylketene acetal yields an α,α-dialkoxyalkyl radical which could undergo a similar frag-

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