siderations and because of a decrease in electronegativity of the phosphorus in the C–P bond due to decrease in s character through hybridization with p and d orbitals. Further studies of pentavalent phosphorus substituents are of interest. Substituents in such a series should conform to a relationship for $\sigma_{\mathrm{I(X)}}$ and $\sigma_{\mathrm{R(X)}}{}^0$ dependencies similar to that noted above for the tetracoordinated phosphorus substituents.

Restricted Rotation in *t*-Butylcycloalkanes. Effect of Ring Size[1]

F. A. L. Anet, Maurice St. Jacques, and Gwendolyn N. Chmurny

Contribution No. 2183 from the Department of Chemistry, University of California, Los Angeles, California 90024. Received April 1, 1968

Abstract: The low-temperature (−130 to −160°) nmr spectra of the *t*-butyl protons in *t*-butylcycloalkanes (I-*n*, where *n* is the ring size) appear as 2:1 doublets, more or less well resolved, indicating restricted rotation. $\Delta F^{\ddagger}$ for the rotational barriers for I-5 to I-10 were found to vary from 6.0 to 7.8 kcal/mol in the following qualitatively understandable fashion: I-5 ~ I-6 < I-9 ~ I-10 ~ I-7 < I-8. Although a new interpretation of the nmr spectrum at low temperature of *t*-butylcyclooctane is presented, previous conclusions about the conformations of eight-membered rings are unchanged.

Nuclear magnetic resonance has been a valuable tool for the study of restricted rotation about the single bond joining two sp^3 hybridized carbon atoms.[2] Most of this work has involved fluorine resonance and highly substituted ethane derivatives.[3] In our previous nmr work[4] on *t*-butylcyclooctane (I-8), it had appeared that restricted rotation was not the explanation for changes which were observed in the *t*-butyl band at low temperatures. From more recent data discussed below, it is now apparent that these observed spectral changes are caused by rotation of the *t*-butyl group and that the observed rotational barriers for this type of rotation are affected markedly by ring size.

Results and Discussion

The room temperature nmr spectra of *t*-butylcycloalkanes show single sharp bands for the *t*-butyl protons and broad unresolved multiplets for the methylene protons.

In our earlier work[4] on *t*-butylcyclooctane (I-8), it was found that the low-temperature nmr spectrum of the *t*-butyl group was a 2:1 doublet. At that time, this fact was not attributed to restricted rotation because (a) *t*-butylcyclohexane (I-6) did not show a similar change down to −150° and (b) the splitting in the *t*-butyl band of I-8 was accompanied by distinct changes in the ring proton bands. Since rotation of the *t*-butyl group does not affect the chemical shift of the ring protons whereas a ring conformational change can affect the chemical shifts of both bands, the simplest hypothesis is that a ring conformational change is occurring rather than restricted rotation. However, the large splitting (14 Hz) observed in the *t*-butyl band at low temperatures is not in agreement with such a theory, and indeed was described as "puzzling" in the previous work. It is now apparent from our new data that I-6 is not a very good model for I-8 as far as restricted rotation is concerned (Table I) and that, by

Table I. Chemical Shift and $\Delta F^{\ddagger}$ Data for *t*-Butylcycloalkanes

Compd	T_c,[a] °C	*t*-Butyl chemical shift (τ)[b]	Separation of *t*-butyl doublet[c] ν_{AB}, Hz at 60 MHz	$\Delta F^{\ddagger}$,[d] kcal/mol
I-5	*Ca.* −155	9.16	7	*Ca.* 6.0
I-6	*Ca.* −150	9.16	8	*Ca.* 6.3
		9.17[e]	13[e]	. . .
I-7	−126	9.19	11	7.4
I-8	−118	9.21	13.5	7.8
I-9	−130	9.15	10	7.3
I-10	*Ca.* −130	9.15	9	*Ca.* 7.3

[a] Temperature of maximum spectral change. This corresponds roughly to the coalescence temperature for a completely resolved 2:1 doublet. [b] TMS = 10 ppm. These values are weighted average chemical shifts of the 2:1 doublets under the conditions given in Figure 1. [c] At temperatures given in Figure 1. [d] $\Delta F^{\ddagger}$, the Gibb's free energy of activation for rotation of the *t*-butyl group about the $C_\alpha C_{\alpha'}$ bond by 120° in one direction, was calculated from absolute rate theory and rate constants obtained at T_c. Computer calculated spectra derived from these rate constants were in good agreement with experimental spectra in the two cases (I-5 and I-7) where this check was made. Because of varying reference line widths at different temperatures, the rate constants especially for I-5, I-6, and I-10 are only approximate; however, $\Delta F^{\ddagger}$ should be accurate to ±0.1 kcal/mol for I-7, I-8, and I-9 and to ±0.2 kcal/mol for I-5, I-6, and I-10. [e] 100 MHz. This spectrum was obtained by Y. Ogawa on a 4 H 100 spectrometer through the courtesy of Jeolco.

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(1) This research was supported by the National Science Foundation, Grant No. GP6620, the U. S. Public Health Service, Grant No. GM-12769, and by a National Research Council of Canada Scholarship.

(2) (a) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp 377–385; (b) J. D. Roberts, "Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp 58–60, 71–74; (c) R. A. Newmark and C. H. Sederholm, *J. Chem. Phys.*, 43, 602 (1965); (d) J. D. Roberts, Abstracts, 20th National Organic Symposium of the American Chemical Society, Burlington, Vt., June 1967.

(3) The only studies of barriers to rotation in ethane derivatives by proton nmr appear to be on 2,2,3,3-tetrabromobutane [J. D. Roberts, Abstracts, 19th National Organic Symposium of the American Chemical Society, Tempe, Ariz., June 1965]; on 1-fluoro-1,1,2,2-tetrabromoethane [G. Govil and H. J. Bernstein, *J. Chem. Phys.*, 47, 2818 (1967)]; on 1-fluoro-1,1,2,2-tetrachloroethane [T. D. Alger, H. S. Gutowsky, and R. L. Vold, *ibid.*, 3130 (1967)]; and on the adduct of tetrafluorobenzyne to *t*-butylbenzene [J. P. N. Brewer, H. Heaney, and B. A. Marples, *Chem. Commun.*, 27 (1967)].

(4) F. A. L. Anet and M. St. Jacques, *J. Amer. Chem. Soc.*, **88**, 2586 (1966).

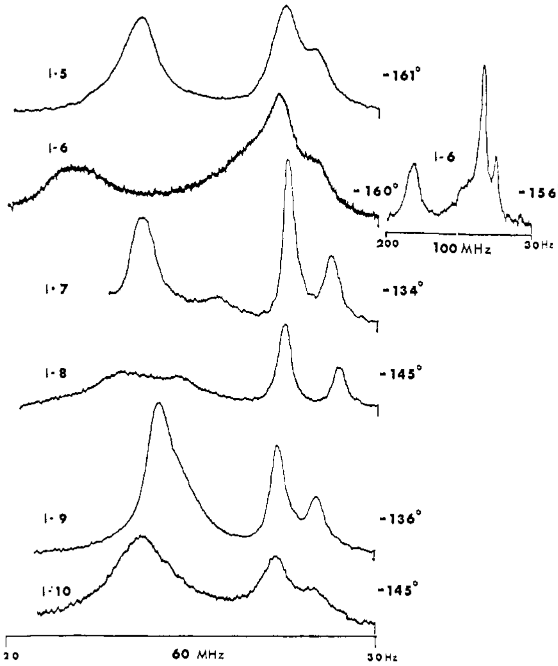


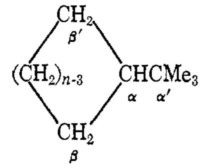
Figure 1. Proton nmr spectra (60 and 100 MHz) of *t*-butylcycloalkanes (I-*n*, *n*-membered ring) at low temperatures. The scale is in hertz downfield from tetramethylsilane (TMS). The *t*-butyl 2:1 doublet is at high field in each spectrum.

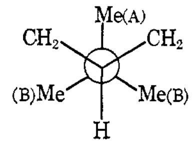
coincidence, ring inversion and restricted rotation have nearly the same rate constants in I-8.

In view of the differences between the nmr spectra of I-6 and I-8 at low temperatures, an investigation of the low-temperature nmr spectra of other *t*-butylcycloalkanes appeared to be important for a better understanding of the problem.

At sufficiently low temperatures, the *t*-butyl bands for all *t*-butylcycloalkanes, I-5 through I-10, are split into 2:1 doublets, more or less well resolved (Figure 1 and Table I). For example, at 60 MHz and −160°, the *t*-butyl protons of *t*-butylcyclohexane (I-6) give a broad band with an inflection on the upfield side of the band. At 100 MHz and −156°, a 2:1 doublet is partially resolved (Figure 1). The larger membered rings (I-7, I-8, and I-9) give better resolved 2:1 doublets than the smaller membered rings (I-5 and I-6), in part because of a larger doublet separation, but mainly because of a higher barrier to restricted rotation, which does not demand very low temperatures for the nmr measurements. All the lines in the spectra (and in TMS) broaden at very low temperatures independently of the presence of any intramolecular exchange process, such as restricted rotation or ring pseudorotation, because of the increased viscosity of the solvent and the the consequently increased effectiveness of dipole-dipole relaxation.

The 2:1 doublet observed at low temperatures must result from the staggered arrangement about the $C_\alpha C_{\alpha'}$ bond, as shown in the accompanying Newman projection. The methyl group (A) *trans* to the hydrogen on C_α is at higher field than the other two methyl groups (B) in all of the compounds. For *t*-butylcyclohexane, calculations based on magnetic anisotropies of C–C and C–H bonds were carried out. The screening constants (σ) for A and B methyl protons were calculated using the McConnell equation as modified by ApSimon and coworkers.[5] The values of the angles and distances used in these calculations were obtained by measurements on a Fieser molecular model of *t*-butylcyclohexane in a fixed and completely staggered conformation. The constants[5] used for magnetic susceptibilities (χ_L and χ_T), magnetic anisotropies ($\Delta\chi$), and half the length of the electric dipole (S) are given as follows: $\Delta_\chi^{CC} = +13.98 \times 10^{-30}$ cm^3/molecule, $\Delta_\chi^{CH} = +11.00 \times 10^{-30}$ cm^3/molecule; $\chi_L^{CC} = +3.15 \times 10^{-30}$ cm^3/molecule, $\chi_L^{CH} = +0.92 \times 10^{-30}$ cm^3/molecule; $\chi_T^{CC} = -10.83 \times 10^{-30}$ cm^3/molecule, $\chi_T^{CH} = -10.08 \times 10^{-30}$ cm^3/molecule; $S^{CC} = 0.6$ Å, $S^{CH} = 0.25$ Å.





Values for σ_A and σ_B were caluclated for each proton in the *t*-butyl group with respect to every C–C and C–H bond in the molecule with the exception of the $C_\alpha C_{\alpha'}$ bond and the bonds within the *t*-butyl group. The contributions from the latter bonds were assumed to be the same for both types of methyl group. The sums of σ_{CC} and σ_{CH} for each proton in the A methyl, and similarly in the B methyl groups, were then averaged to obtain σ_A and σ_B of −0.02 and +0.20 ppm, respectively. Thus at 60 MHz, the A methyl band is calculated to be 13 Hz to low field of the B methyl band, a result not in agreement with experiment.[6]

The transition state for restricted rotation is expected to have an eclipsed arrangement about $C_\alpha C_{\alpha'}$, resulting in two methyl-β-methylene and one methyl-C_αH eclipsed interactions. Since the conformation of butane in which the two methyl groups are eclipsed has been estimated[7] to be from 4.4 to 6.1 kcal/mol higher in energy than the staggered conformation of lowest energy, the eclipsing energy of a pair of methyl groups is this value minus the eclipsing energy of two pairs of hydrogens (2 × 1.0 kcal/mol) and is thus 2.4–4.1 kcal/mol. This value should be a fair approximation for the eclipsed methyl-β-methylene interaction in our system. Similarly, the methyl-C_αH eclipsed interaction can be estimated to be 1.2 kcal/mol. The total eclipsing energy of the transition state for restricted rotation is then predicted to be 2(2.4–4.1) + 1.2, or 6.0–9.4 kcal/mol. By comparison, the ground-state conformation for restricted rotation has four *gauche* methyl-β-methylene interactions worth 4(0.8), or 3.2 kcal/mol. The barrier to rotation is therefore predicted to be 2.8–6.2 kcal/mol. The rotational barriers given

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[5] The treatment does not make use of the point-dipole approximation: J. W. ApSimon, W. G. Craig, P. V. Demarco, D. W. Mathieson, L. Saunders, and W. B. Whalley, *Tetrahedron*, 2339 (1967).

[6] The molecular models used in our calculation have tetrahedral bond angles, whereas it is known that cyclohexane has bond angles of 111.6°: M. Davis and O. Hassel, *Acta. Chem. Scand.*, 17, 1181 (1963). It is not expected that these bond angle variations will greatly affect the calculations. The values of the magnetic anisotropies are not firmly established and could also lead to error. The effect of methyl groups on cyclohexane chemical shifts, it should be noted, are *not* readily understandable (A. Segre and J. I. Musher, *J. Amer. Chem. Soc.*, **89**, 706 (1967), and N. Muller, personal communication).

[7] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, Inc., New York, N. Y., 1965, p 9.

in Table I are in agreement with the upper extreme of the predicted range of values.

The data show that the barriers to restricted rotation in the *t*-butylcycloalkanes depend very markedly on ring size. The methyl-β-methylene interactions should increase with (a) increasing internal angle ($C_\beta C_\alpha C_{\beta'}$) and (b) increasing eclipsing of the $C_\alpha C_{\alpha'}$ bond with the β-methylene bonds. The internal angle increases in the order I-5 < I-6 < I-7 < I-8–I-10, while eclipsing is very small in I-6, and is appreciable in the other compounds. Although the strains in the transition states will distribute themselves so that the total strain is a minimum, the variation of the barrier to rotation with ring size, namely, I-5 $\sim$ I-6 < I-9 $\sim$ I-10 $\sim$ I-7 < I-8 is therefore understandable in a qualitative fashion. Barriers for comparison with those found in this work in principle can be calculated using semiempirical computer-based methods.[8] Hendrickson has recently calculated conformational parameters for substituted six–ten-membered cycloalkanes.[8d]

The *t*-butyl bands in the low-temperature spectra of I-10 are broader than expected from line broadening (Figure 1). This is possibly indicative of a barrier for some type of ring process, *e.g.*, pseudorotation, and it is planned to investigate this point further through the examination of the nmr spectra of deuterated derivatives of I-10.

The mass spectra at 70 eV of the *t*-butylcycloalkanes I-6 through I-10 show very small molecular ion peaks. Intense peaks occur at *m/e* 57 for the *t*-butyl ion and at 56 for the isobutylene ion. The first peak of appreciable intensity following the molecular ion peak corresponds to the loss of *t*-butyl from the parent ion and is accompanied by a second peak of equal or greater intensity which corresponds to a further loss of molecular hydrogen. Similar groupings occur at *m/e* which correspond to $M - [C_4H_9 \text{ plus } (CH_2)_n]$. The fragmentation pattern where $n = 1$ is nearly negligible in I-10 and increases in intensity so that it is equal to $M - C_4H_9$ in I-6. As is expected at 70 eV, the smaller fragmentation patterns dominate the mass spectra for all of the *t*-butylcycloalkanes.

Experimental Section

In the syntheses described here, no attempts were made to optimize yields since only a few milligrams of each hydrocarbon were required. Melting points are uncorrected. All infrared spectra were recorded on a Beckman IR-5 spectrophotometer on a Nujol mull of the sample. Mass spectra were obtained on an Associated Electronics Instruments mass spectrometer MS-9 at 70 and 10–12 eV by Miss Sharon Jones. Vapor phase chromatography (vpc) examinations were obtained on an Aerograph A90-P3 instrument with a 5-ft Carbowax 20M column (30% on Chromosorb P, HMDS, 60–80 mesh) unless otherwise stated. Carbon, hydrogen analyses were obtained at this University by Miss Heather King.

Nuclear magnetic resonance (nmr) spectra were obtained on a modified[9] Varian HR 60 spectrometer operating at 60 MHz. Samples for nmr spectra were *ca.* 3% (by volume) solutions of the *t*-butylcycloalkanes in a 2:1 mixture of vinyl chloride and chlorodifluoromethane, mp −159.9 and −160°, respectively. In order to obtain a tetramethylsilane (TMS) peak of approximately the same height as the *t*-butyl peak, calculated amounts of TMS were added by means of a 1.0-mm capillary pipet as a 10% solution in carbon disulfide. The samples were then degassed and sealed.[9] The relative areas for the *t*-butyl protons and the combined methylene and methyne protons in all of the nmr spectra for the cycloalkanes are of the right order of magnitude, but exact numbers are not given because of undetermined overlap of the methylene proton and the *t*-butyl band. This is especially important at low temperatures and is in part responsible for the approximation of 2:1 doublets for the *t*-butyl bands.

Calculations of screening constants were carried out on an Olivetti Underwood Programma 101 using eq 5 of ApSimon and coworkers.[5] Calculations of nmr spectra were carried out by means of the multisite FORTRAN program of Saunders[10] modified for use on an IBM 360 by Mark Henrichs of our laboratory.

***t*-Butylcyclohexane (I-6) and 5-*t*-butylcyclohexanone** were obtained from Aldrich and used directly. 5-*t*-Butylcyclooctanol[11] was a gift from Professor N. L. Allinger. Toluenesulfonyl chloride, hydrazine hydrate, and diethylene glycol (Matheson Coleman and Bell) were used without further purification. Metal hydrides, lithium aluminum hydride, Baker Analyzed reagent petroleum ether, Mallinckrodt Chemical Works analytical reagent ether, and Linde 4A Molecular Sieves were also used directly. Pyridine and tetrahydrofuran (Matheson Coleman and Bell) were dried by storage over potassium hydroxide pellets and by distillation from lithium aluminum hydride, respectively. Boron trifluoride etherate complex (Allied Chemicals) was purified by vacuum distillation and stored under nitrogen prior to use. N-Nitrosomethylurea was prepared according to Arndt.[12] Chlorodifluoromethane (CHF_2Cl) and vinyl chloride were obtained in lecture cylinders from Matheson.

Diazomethane. A solution (*ca.* 1.0 *N*) of diazomethane in ether was prepared from N-nitrosomethylurea according to standard procedures[13] from 12 ml of 50% potassium hydroxide, 20 ml of pure ether, and 4.2 g (40.7 mmol) of N-nitrosomethylurea.

***t*-Butylcyclopentane (I-5).** 3-*t*-Butyladipic acid was prepared according to the published procedure for cleavage of cyclohexanol[14] from 793 mg (5.13 mmol) of 4-*t*-butylcyclohexanone, 2.1 g (16.6 mmol) of 50% nitric acid, and 1 mg of ammonium (*meta*) vanadate catalyst. The 3-*t*-butyladipic acid was isolated in pentane to yield 366.3 mg (1.81 mmol, 35.4%) of product: mp 108–110° (lit.[15] mp 117°); ir 1710 (C=O), 1690 (C–O broad), and 2550–2750 cm^{-1} (broad acid dimer).[16]

The above diacid was heated with 13.6 mg (0.04 mmol) of barium hydroxide at 265° for 1 hr. Water was added to the cooled mixture and the ketone extracted with ether. After concentration, vpc examination at 165°, flow rate 60 ml/min, showed no 4-*t*-butylcyclohexanone at 8.3 min and a new peak at 4.5 min retention time. The crude mixture was used directly to prepare the hydrocarbon.

t-Butylcyclopentane was obtained by a Wolff–Kishner reduction[17] of the above ether concentrate with 2.5 ml of diethylene glycol, 0.25 ml of hydrazine hydrate, and 0.25 g of potassium hydroxide. Vpc examination at 160°, flow rate 60 ml/min, showed no peak at 4.75 min corresponding to 3-*t*-butylcyclopentanone and a new peak at 1.4 min. This peak was collected to yield 50.3 mg of pure hydrocarbon.

Anal. Calcd for C_9H_{18}: C, 85.63; H, 14.37. Found: C, 85.42; H, 14.43.

***t*-Butylcycloheptane (I-7).** To 200 mg (1.30 mmol) of 4-*t*-butylcyclohexanone in 3–5 ml of ether was added 0.08 ml (*ca.* two drops) of boron trifluoride–etherate complex. To this stirred solution at room temperature was added in small portions diazomethane solution (*ca.* 20 mmol, theoretical from N-nitrosomethylurea). It was necessary to add the boron trifluoride catalyst immediately prior to the diazomethane addition to prevent apparent self con-

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(8) J. B. Hendrickson, *J. Amer. Chem. Soc.*, **86**, 4854 (1964); (b) *ibid.*, **89**, 7036 (1967); (c) *ibid.*, **89**, 7043 (1967); (d) *ibid.*, **89**, 7047 (1967); (e) K. B. Wiberg, *ibid.*, **87**, 1070 (1965); (f) N. L. Allinger, M. A. Miller, F. A. Van Catledge, and J. A. Hirsch, *ibid.*, **89**, 4345 (1967). A rather large number of conformations have to be considered in such calculations.

(9) F. A. L. Anet and A. J. Bourn, *ibid.*, **89**, 760 (1967).

(10) M. Saunders, *Tetrahedron Lett.*, 1699 (1963); from line width theory of P. W. Anderson [*J. Phys. Soc. Jap.*, **9**, 16 (1954)] mathematically modified by R. A. Sack, *Mol. Phys.*, **1**, 163 (1958).

(11) N. L. Allinger and S. Greenberg, *J. Amer. Chem. Soc.*, **84**, 2394 (1962).

(12) F. Arndt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p 461.

(13) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," John Wiley and Sons, Inc., New York, N. Y., 1967, pp 191–195.

(14) B. A. Ellis, *Org. Syn.*, 1, 18 (1932).

(15) H. Pines and V. N. Ipatieff, *J. Amer. Chem. Soc.*, **61**, 2728 (1939). These authors also prepared *t*-butylcyclopentane by a different route.

(16) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1959, Chapter 10.

(17) Reference 13, pp 435–436.

densations of the ketone catalyzed by the boron trifluoride complex. Vpc examination of the ether concentrate from the above reaction at 195°, flow rate 60 ml/min, showed 64% of the seven-membered ketone and 36% of the six (relative areas) at 12.2 and 8.4 min retention time, respectively. A small amount of the eight-membered ketone was also present.

The above ketone mixture was reduced under Wolff-Kishner conditions with 0.19 g of potassium hydroxide, 0.19 ml of hydrazine hydrate, and 1.9 ml of diethylene glycol for 1 hr at 145° followed by a 4 hr reflux at 195-200°. The reaction was worked up with 15 ml of water followed by extraction with ether. Vpc examination of the concentrated ether extracts showed no starting ketones but two new major peaks in relative amounts similar to those for the ketone mixture at shorter retention times, 69% of I-7 (3.0 min) and 31% of I-6 (1.8 min). (A small amount of I-8 (4.6 min) was also present.) Collection by vpc at 180° gave *ca.* 20 mg of I-6 and *ca.* 45 mg of I-7. The mass spectra of I-6 and I-7 gave correct parent ion peaks and fragmentation patterns: *m/e* 140 and 83 for I-6 and 154 and 97 for I-7.

Anal. Calcd for $C_{11}H_{22}$: C, 85.63; H, 14.37. Found: C, 85.78; H, 14.56.

***t*-Butylcyclooctane (I-8), *t*-Butylcyclononane (I-9), and *t*-Butylcyclodecane (I-10).** These hydrocarbons were prepared according to the following route as a mixture and separated in the last stage by vpc. 5-*t*-Butylcyclooctanone was obtained from 5-*t*-butylcyclooctanol[11] by a Brown chromic acid oxidation.[18] The alcohol, 1.14 g (6.2 mmol), was oxidized with 1.4 g of sodium dichromate, 1.0 ml of concentrated sulfuric acid, and 6 ml of water at room temperature for 2.5 hr. Vpc examination of the concentrated ether extracts at 165°, flow rate 60 ml/min, showed no alcohol and a new peak identical with that of a known sample of *t*-butylcyclooctanone[19] at a shorter retention time.

After several attempts at ring expansion, the above mixture was dried over molecular sieves to remove water and ethanol and concentrated to *ca.* 30 ml in ether. Diazomethane from 204 mmol of N-nitrosomethylurea was added to the ketone mixture and 0.5 ml of boron trifluoride–etherate complex (added immediately prior to diazomethane addition; see above). The reaction was vigorous giving large precipitation of polymethylene. Vpc analysis at 215°, flow rate 100 ml/min, gave the following relative areas of ketones: I-8, 43%; I-9, 31%; and I-10, 26% (two peaks slightly resolved, *ca.* 50:50). Some higher homologs were indicated by vpc but were not analyzed for. This mixture of ketones was concentrated by distillation and subjected directly to Wolff-Kishner reduction with 0.82 ml of hydrazine hydrate, 0.82 g of potassium hydroxide, and 8.2 ml of diethylene glycol at 143-145° for 2 hr followed by reflux at 195° for 6 hr. To the cool reaction mixture was added 25 ml of water and the reaction worked up as before. Vpc examination of the concentrated reaction mixture at 215°, flow rate 100 ml/min, showed no peaks corresponding to unreacted starting material at 8.8, 12.3, and 18.2 min and three new peaks at 1.9, 2.9, and 4.2 min for I-8, I-9, and I-10, respectively. Collection of these peaks on the same column at 180° gave 89.5 mg of I-8, 66.9 mg of I-9, and 48.2 mg of I-10. A small amount of a higher homolog believed to be the eleven-membered ring hydrocarbon was also collected. The mass spectra of I-8, I-9, and I-10 gave correct parent ion peaks and fragmentation patterns: *m/e* 168 and 111 (I-8), 182 and 125 (I-9), and 196 and 139 (I-10).

Anal. Calcd for C_nH_{2n}: C, 85.63; H, 14.37. Found for I-8; C, 85.59; H, 14.28. Found for I-9: C, 85.70; H, 14.38. Found for I-10: C, 85.66; H, 14.41.

***t*-Butylcyclooctane (I-8) (Alternate Preparation).** To 0.3 g (1.63 mmol) of 5-*t*-butylcyclooctanol[11] in 5 ml of dry pyridine was added 0.40 g (2.20 mmol) of *p*-toluenesulfonyl chloride and the solution was allowed to stand at 0° for 24 hr. Following the usual work-up, the ether was evaporated and 10 ml of tetrahydrofuran was added. The solution was added dropwise to a slurry of 0.70 g (18.5 mmol) of lithium aluminum hydride in 15 ml of THF and the mixture was refluxed for 47 hr. To the cool solution was added 35 ml of 6 *N* hydrochloric acid followed by 10 ml of petroleum ether (bp 40-60°). The ether phase was separated, washed with water, and dried over magnesium sulfate. After concentration under reduced pressure, the *t*-butylcyclooctane was collected by vpc on a 10-ft Silicone GE SF-96 column (30% on Chromosorb P, HMDS, 60-80 mesh) at 180°. The nmr spectrum of this compound (10% in carbon disulfide) was identical with that obtained as reduced starting material in the preparation of the *t*-butylcycloalkanes I-8, I-9, and I-10 given above.

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[18] H. C. Brown and C. P. Garg, *J. Amer. Chem. Soc.*, **83**, 2952 (1961).

[19] Similarly prepared from *t*-butylcyclooctanol by M. St. Jacques, Ph.D. Thesis, University of California at Los Angeles, Los Angeles, Calif., 1967, p 244: ir 1700 cm^{-1} (lit.[11] bp 113-115° (7 mm)); $n^{26}D$ 1.4714.

Disilaoxadiazines. Silyl Tautomerism in Cyclic Silylamides Involving Expanded-Octet Silicon

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Contribution from the General Electric Research and Development Center, Schenectady, New York. *Received February 19, 1968*

Abstract: 2,4-Disila-1,3,5-oxadiazine derivatives have been prepared by reaction of dimethyl-, methylphenyl-, methylmethoxy-, and diphenyldichlorosilane with acetamide and/or benzamide. The new six-membered heterocycles contain two silyl and two amide groups, one of the latter in imino ether form. Protonic reagents displace two molecules of amide from silicon in successive steps. The disilaoxadiazines undergo reversible intramolecular rearrangements at two temperature levels. At 20-50°, depending on the nature of the substituents, amide and imino ether moieties interconvert at a rate causing coalescence of their respective nmr signals. A temperature increase of 50-80° leads to coalescence of signals due to substituents on silicon. The phenomena suggest coordination of the amide moieties with one of the silicon atoms in an expanded shell, the other silicon being tetracoordinated. At higher temperatures, the silicon moieties interconvert reversibly.

The structure of silylamides has been a subject of controversy for a number of years. Probing of the alternatives—N-silylamide or O-silylimino ether—by chemical means is unsuitable because tautomerizations of intermediates and products are likely to occur, leaving the issue to spectroscopic arguments. Evidence cited in favor of the N-silylated amide form is based primarily on infrared spectra,[1] whereas ultraviolet absorption data of aromatic silylamides have been interpreted as evidence for O-silylated enol struc-

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[1] W. Giessler, Inaugural Dissertation, Universität Köln, Germany, 1963.