centrated to a residue from which boric acid was removed *in vacuo* as its methyl ester. Acetylation with acetic anhydride–pyridine then gave crystalline *myo*-inositol hexaacetate which was identified by its melting point and infrared spectrum and by comparison with an authentic specimen. A sample of the hexaacetate was deacetylated and converted into the TMS derivative which proved to be indistinguishable, on glpc, from an authentic sample of the TMS derivative of *myo*-inositol (**8**).

The formation of *scyllo*-inositol (**7**) and of *myo*-inositol (**8**) unequivocally identifies the product from the alkaline treatment of **5** as *myo*-inosose-2 (**6**). The ease with which **5** cyclizes to **6** lends support to the proposed pathway for the biosynthesis of *myo*-inositol, and it is interesting to note that, while *scyllo*-inositol was first discovered in nature 110 years ago, the presence of *myo*-inosose-2 in a biological system was first reported only this year, Sherman and his coworkers[16] finding it, together with *scyllo*-inositol, in rat sciatic nerve and calf brain.

Acknowledgment. We are indebted to Dr. F. Eisenberg, Jr., of this Institute for a sample of authentic *scyllo*-inositol and to Dr. A. J. Fatiadi of the National Bureau of Standards for a specimen of *myo*-inosose-2.

(16) W. R. Sherman, M. A. Stewart, P. C. Simpson, and S. L. Goodwin, *Biochemistry*, 7, 819 (1968).

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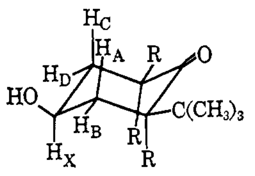
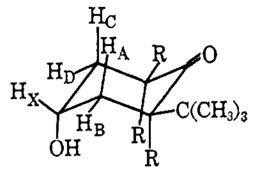
Conformational Studies. X. Census of Nonchair Conformations of 2-*t*-Butylcyclohexanones[1]

Sir:

Optical rotatory dispersion[2] and circular dichroism[3] studies of 2-*t*-butylcyclohexanone have been interpreted without invoking nonchair conformations.[2,3] However, Allinger[4] has concluded from estimates of nonbonded group interactions that "the amount of compound in the boat form in 2-*t*-butylcyclohexanone is ... appreciable," implying a need for reinterpretation of the optical results.[2,3] We wish to report infrared and nmr studies of *cis*- and *trans*-2-*t*-butyl-4-hydroxycylohexanone (**1** and **2**) which allow limits to be set upon nonchair populations of **1** and **2** and from which we infer by analogy that nonchair populations are *not* appreciable for 2-*t*-butylcyclohexanone.

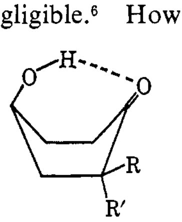


1, R = H
3, R = D



2, R = H
4, R = D

No evidence of intramolecular hydrogen bonding was detected by infrared spectroscopy for either **1** or **2**.[5] We conclude that the populations of boat conformations $\mathbf{1b}_0$ and $\mathbf{2b}_0$ are negligible.[6] However, for **1** and **2**, there are five other boat ($\mathbf{b}_\psi$) and six twist ($\mathbf{t}_\psi$) conformations to be considered in which significant intramolecular hydrogen bonding is *not* possible. Defining boat conformation $\mathbf{b}_0$ as the $\psi = 0°$ (and 360°) point of the nonchair pseudo-rotational cycle, each nonchair conformation may be identified.



$\mathbf{1b}_0$, R = C(CH$_3$)$_3$; R' = H
$\mathbf{2b}_0$, R = H; R' = C(CH$_3$)$_3$

Examination of Dreiding molecular models suggests that steric strain is severe for **1** when ψ is 210–330° and for **2** when ψ is 30–90°.[7] Nonchair conformations within these ψ ranges for **1** and **2** undoubtedly have negligible populations.[7] In estimating population limits for the remaining possible conformations, nmr studies of **1** and **2** as their 2,6,6-d_3 derivatives (**3** and **4**) have been most informative.[8] These compounds afford ABCDX spin systems. The *cis* isomer **3** gives a first-order-like triplet of triplets for the C_4 X-proton resonance, band width, *W* (separation between the outer lines of the multiplet), 29.6 ± 0.1 Hz in benzene and 30.2 ± 0.2 Hz in methanol-d_4. Computer analysis shows the spectrum of **3** in methanol-d_4 solution to be consistent with $J_{AX} = J_{CX} = 10.7$, $J_{BX} = 4.3$, and $J_{DX} = 4.5$ Hz.[9]

Compare **3** with *cis,cis*-2,6-dimethyl-4-hydroxycyclohexanone (**5**), for which conformations other than the chair with all three substituents equatorial would be populated negligibly.[10] For **5**, the C_4 X-proton band width is 29.5 ± 0.2 Hz in benzene and 30.2 ± 0.2 Hz in methanol-d_4 solution, the same as for **3** within experimental error. For **3**, the conformations consistent with its observed *W* and *J* values are the chair illustrated for **3**, above, and $\mathbf{3b}_{180}$, with nearly the same dihedral angles

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(1) We wish to thank the National Science Foundation for support of this work.

(2) C. Djerassi, P. A. Hart, and E. J. Warawa, *J. Am. Chem. Soc.*, **86**, 78 (1964).

(3) K. M. Wellman, W. S. Briggs, and C. Djerassi, *ibid.*, **87**, 73 (1965).

(4) N. L. Allinger, H. M. Blatter, L. A. Freiberg, and F. M. Karkowski, *ibid.*, **88**, 2999 (1966).

(5) The experimental procedures used were similar to those reported by R. D. Stolow, *J. Am. Chem. Soc.*, **84**, 686 (1962).

(6) See ref 5, footnote 2.

(7) Boat conformations $\mathbf{1b}_{240}$ and $\mathbf{2b}_{60}$ have the *t*-butyl group in the most strained position; their adjacent twist conformations, $\mathbf{1t}_{210}$, $\mathbf{1t}_{270}$, $\mathbf{2t}_{30}$, and $\mathbf{2t}_{90}$, are also severely strained. In these conformations, *t*-butyl would occupy the C_6-B or C_6-TB 1β(a) positions described for methylcyclohexane by J. B. Hendrickson, *J. Am. Chem. Soc.*, **89**, 7043 (1967). A *t*-butyl group at these positions would experience much more severe repulsive interactions than a methyl group. The 1,3-diaxial-type *t*-butyl–hydroxyl interaction, which would severely destabilize $\mathbf{1b}_{300}$, is only partially relieved in $\mathbf{1t}_{330}$.

(8) We are deeply indebted to Dr. Kenneth Williamson and to Dr. David Nelson for recording spectra of **3** and **4** at 100 MHz by use of Varian HA-100 spectrometers. The hydroxyl proton was observed in each case as a sharp singlet (rapid exchange).

(9) Estimated probable error ±0.2 Hz. LAOCOON I and II and NMRIT programs were used. See J. D. Swalen, *Progr. Nucl. Magnetic Resonance Spectry.*, **1**, 205 (1966). The sum of the vicinal coupling constants equals the experimental X-proton band width. Expected changes in vicinal coupling constants with changes in HCCH dihedral angle (ω) were estimated taking $J = A\cos^2\omega - B\cos\omega + C$; $A = 10$, $B = 1$, and $C = 0$. See C. Altona, H. R. Buys, H. J. Hageman, and E. Havinga, *Tetrahedron*, **23**, 2265 (1967).

(10) M. Litchman prepared **5**, mp 65.8–66.2°, by Jones oxidation of *cis,cis,cis*-2,6-dimethyl-1,4-cyclohexanediol,[11] mp 139.5–140°.

(11) R. D. Stolow and R. R. Krikorian, unpublished work.

about the C_3–C_4 and C_4–C_5 bonds. The diaxial chair and conformations $\mathbf{3b}_{210}$ through $\mathbf{3b}_{330}$ (as for **1**)[7] are severely strained and, therefore, negligibly populated. For $\mathbf{3b}_0$ through $\mathbf{3b}_{120}$, we expect $0 \lesssim J_{CX} < 4$ Hz. A total population of more than 4% of $\mathbf{3b}_0$ through $\mathbf{3b}_{120}$ would be detected as a significant decrease in W compared to **5** and/or as an increase in $|J_{AX} - J_{CX}|$ and/or $|J_{BX} - J_{DX}|$. Estimating for $\mathbf{3t}_{150}$, $\Delta J_1 = J_{AX} - J_{CX} > 2.6$ Hz and $\Delta J_2 = J_{DX} - J_{BX} > 2.6$ Hz, then a population of 15% or more of $\mathbf{3t}_{150}$ would give $\Delta J_1 \approx \Delta J_2 \gtrsim 0.4$ Hz, which is *not* observed. Furthermore, computer analysis shows that 10% or more of $\mathbf{3t}_{150}$ would produce a detectable change in line shape within the X-proton multiplet, which is *not* observed. Since steric interactions present in boat $\mathbf{3b}_{180}$ are relaxed upon pseudorotation to $\mathbf{3t}_{150}$, the population of $\mathbf{3b}_{180}$ should be much *less* than the 10% limit set for $\mathbf{3t}_{150}$.[12] Therefore, the nonchair population of **3** is *small*, probably less than 10%.

The *trans* isomer **4** gives a quintet for the C_4 X-proton resonance, $W = 12.0 \pm 0.2$ Hz, in methanol-d_4 solution. Computer analysis shows the spectrum to be consistent with $J_{AX} = J_{CX} = 2.7$ Hz, $J_{BX} = 3.2$ Hz, and $J_{DX} = 3.4$ Hz.[9] One could compare **4** with *cis*-4-*t*-butylcyclohexanol-3,3,4,5,5-d_5 (**6**), which gives $W = 11.4$ Hz for the C_1 proton band width in carbon tetrachloride solution.[13] If W were 11.4 Hz for the chair conformation of **4** with hydroxyl axial (illustrated above), then, for the other chair and $\mathbf{4b}_{120}$ through $\mathbf{4b}_{240}$ ($W > 25$ Hz), the total population would be *less* than 6%. As for **2**, above,[7] $\mathbf{4b}_0$ through $\mathbf{4t}_{90}$ are populated negligibly (no hydrogen bond, or severe strain). For $\mathbf{4t}_{270}$ through $\mathbf{4t}_{330}$, we expect $J_{CX} > 6.0$ Hz. Since $J_{CX} = 2.7 \pm 0.2$ Hz, observed for **4**, is not larger than the corresponding coupling constant for **6**,[13] then the total population of $\mathbf{4t}_{270}$ through $\mathbf{4t}_{330}$ should be less than 10%. The negligible values observed for $|J_{AX} - J_{CX}|$ and $|J_{BX} - J_{DX}|$ confirm this limit. Therefore, the nonchair population of **4** is *small*, probably less than 10%. We suggest extension of this conclusion to 2-*t*-butylcyclohexanone.

[12] It would be unreasonable to suggest special stability for $\mathbf{3b}_{180}$, since it differs from $\mathbf{2b}_0$ only in configuration at C_4, and the latter, which could be stabilized further by intramolecular hydrogen bonding, was not detected in infrared studies of **2** (see above).

[13] F. A. L. Anet, *J. Am. Chem. Soc.*, **84**, 1053 (1962).

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Photolysis of Benzene Vapor. Benzvalene Formation at Wavelengths 2537–2370 Å[1]

Sir:

Although benzene irradiated at 2537 Å in the liquid phase and in solution is known to undergo isomerizations to yield fulvene[2] and benzvalene[3] (tricyclo[3.1.0.0^{2,6}]hex-3-ene), benzene vapor has been considered[4] to be virtually inert to radiation of this wavelength. We have recently shown,[5] however, that benzene-1,3,5-d_3 rearranges to the 1,2,4 isomer at 2537 Å in the vapor phase and have suggested an excited benzvalene intermediate, formed with $\Phi = 0.03$. We now wish to report that benzvalene is indeed formed by photolysis of benzene vapor at 2537 Å and that, in the presence of additives which facilitate its vibrational relaxation and prevent its benzene-photosensitized destruction, steady-state concentrations greater than 1% of the benzene can be attained.

We have investigated the photolysis of benzvalene and benzene in the presence of added gases at 2537 Å and have studied the wavelength dependence of benzvalene formation and other processes in benzene. Photolyses were performed in a cylindrical quartz cell, 2 cm in diameter and 10 cm long, fitted with Teflon stopcocks. The cell was filled by flushing with the appropriate gas or gas mixture; benzvalene samples were introduced as effluent from a gas-chromatographic column.[3] Benzene (*ca.* 4 μl) was added from a microsyringe just before closing the stopcocks. For 2537-Å irradiations, a General Electric G8T5 lamp fitted with a Vycor 7910 shield was mounted parallel to the axis of the cell. For other wavelengths, a Bausch and Lomb SP-200 super pressure mercury lamp and high-intensity grating monochromator (nominal bandpass 32 Å) was used.

A difficulty encountered in working with benzvalene vapor was its rapid isomerization to fulvene in freshly flamed quartz cells. In a cell previously conditioned with benzvalene, *e.g.*, by photolysis of benzene under appropriate conditions, benzvalene was stable, however, and exhibited a characteristic banded absorption spectrum with peaks at 2172, 2182, 2212, 2222, 2256, and 2266 Å (ϵ_{2172} ~4000, ϵ_{2573} ~300). Irradiation of benzvalene (0.1 torr) in 1 atm of N_2 at 2537 Å results in conversion ($\Phi \sim 0.4$) to benzene and fulvene in a ratio ~3 : 1. Under our conditions one-third was consumed in 5 min. In the presence of 20 torr of benzene, the benzvalene disappeared 50 times as rapidly, $\Phi \sim 0.3$, indicating very efficient energy transfer from benzene to benzvalene. Addition of 25 torr of *cis*-2-butene resulted in a 20-fold decrease in the rate of the benzene-sensitized disappearance. Since butene at this pressure does not quench benzene fluorescence,[6] the benzvalene disappearance must be triplet-sensitized; benzene triplets apparently transfer their energy to benzvalene about ten times as efficiently as to butene.

When benzene vapor is irradiated at 2537 Å in the absence of triplet quenchers, benzvalene is barely detectable[3] by gas chromatography. Its steady-state concentration, relative to benzene, is only 0.002% for 25 torr of benzene in 1 atm of N_2 and 0.004% in 1 atm of neopentane. In the presence of 25 torr of *cis*-2-butene, the steady-state concentrations increase markedly, to 0.04% in N_2 and 0.3% in neopentane. At these concentrations it was possible to confirm that the product was benzvalene, both by its characteristic vapor-phase uv absorption and by its reaction[3] with acidified methanol to form 4- and 6-methoxybicyclo[3.1.0]hex-2-enes. In the neopentane–butene mixture, benzvalene production measured by gas chromatography at an early stage corresponds to $\Phi \sim 0.02$. When benzene is irradiated in 1

[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

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