fluoride in methylene chloride at 0° led to efficient cyclization to tricyclic product. The ketone **13** so obtained was isolated in pure form[8] by preparative glpc and converted to *dl*-cedrol **14** by treatment with methyllithium.[4] Comparison of infrared and nmr spectra and glpc behavior of the synthetic product with natural cedrol confirmed the assigned structure **14**.[15]

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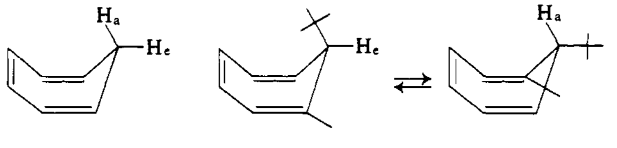
Hindered Ring Inversion of 1-Methyl-7-*t*-butylcycloheptatriene

Sir:

Nuclear magnetic resonance (nmr) spectroscopy has been especially fruitful in delineating not only the intimate structure of cycloheptatriene (**1**)[1,2] and its derivatives,[3-5] but also their energy barrier(s) and rates of interconversion. Whereas, from the studies of Anet[1] and Jensen,[2] extremely low temperatures (−170°) are necessary to slow the interconversion of **1**, we wish to report our studies of a simple derivative of **1** which, because of severe nonbonded interactions, undergoes *slow inversion at room temperature* and which shows further interesting spectral features.



1 **2a** **2b**

Reaction of methyltropylium tetrafluoroborate with *t*-butyllithium[4b,6] gave as the minor product 1-methyl-7-*t*-butyl-1,3,5-cycloheptatriene (**2**).[7,8] The room temperature nmr spectrum[10] of this material exhibited (in addition to complex resonances for the olefinic protons) a broad absorption for the 7-*t*-butyl group centered at τ 9.17 and a singlet at τ 8.06 for the 1-methyl group of **2** (Figure 1A). When the temperature of the sample is progressively lowered, notable changes occur in the spectrum. More specifically, the *t*-butyl resonance sharpens and gives rise to two singlets of unequal intensity at τ 8.94 and 9.23 (ratio of the area of the low-field signal to that of the high-field signal 23:77), while the 1-methyl proton region under-

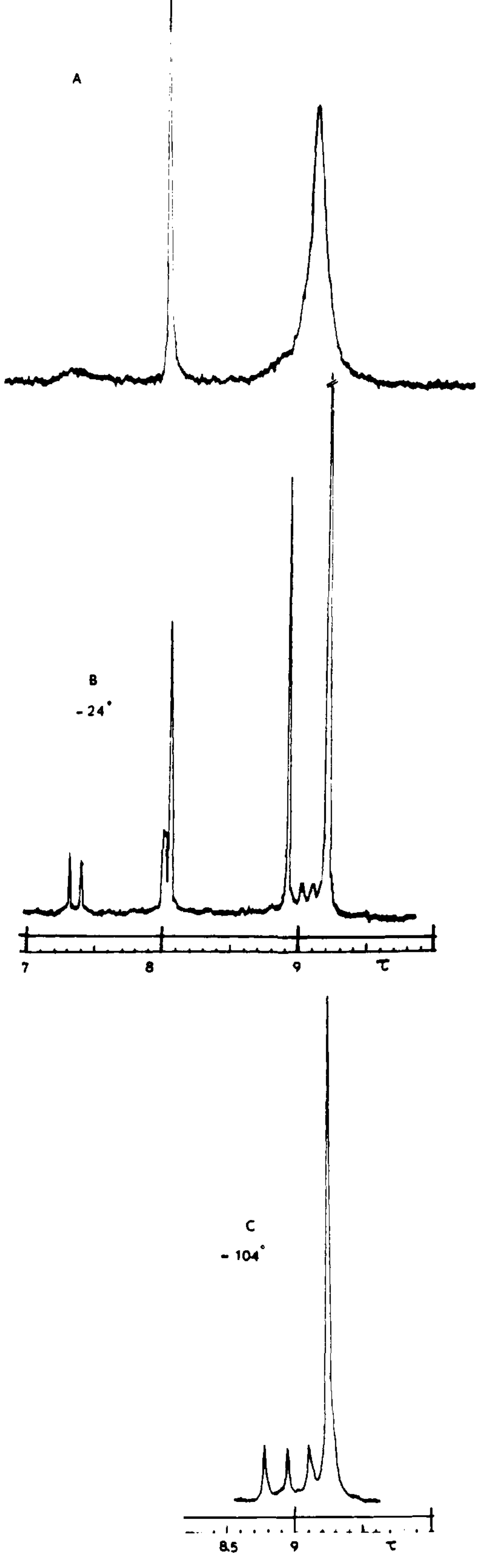


Figure 1. Partial 100-Mc spectra of **2** at different temperatures.

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(1) F. A. L. Anet, *J. Am. Chem. Soc.*, **86**, 458 (1964).

(2) F. R. Jensen and L. A. Smith, *ibid.*, **86**, 956 (1964).

(3) K. Conrow, M. E. Howden, and D. Davis, *ibid.*, **85**, 1929 (1963).

(4) (a) J. B. Lambert, L. J. Durham, P. Lepoutere, and J. D. Roberts, *ibid.*, **87**, 3896 (1965); (b) H. Kessler and E. Muller, *Z. Naturforsch.*, **22b**, 283 (1967); (c) H. Gunther and H.H. Hinrichs, *Tetrahedron Letters*, 797 (1966); (d) K. W. Egger and W. R. Moser, *J. Phys. Chem.*, **71**, 3699 (1967); (e) J. A. Berson and M. R. Willcott, III, *J. Am. Chem. Soc.*, **88**, 2494 (1966).

(5) H. Gunther, M. Gorlitz, and H. H. Hinrichs, *Tetrahedron*, **24**, 5565 (1968).

(6) W. von E. Doering and H. Krauch, *Angew. Chem.*, **68**, 661 (1956).

(7) A satisfactory analysis was obtained for this material.

(8) 1-Methyl-7-*t*-butyl-1,3,5-cycloheptatriene (**2**) was isolated from the reaction mixture by preparative gas chromatography on an 18% γ-methyl-γ-nitropimelonitrile column.[9] The experimental details and product distribution for this and other reactions of alkyltropylium ions with organolithium compounds will be reported in the full paper.

(9) K. Conrow, *J. Am. Chem. Soc.*, **83**, 2343 (1961).

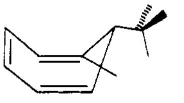
(10) Nmr spectra were measured on a Varian HA-100 spectrometer equipped with a variable-temperature probe. All spectra were obtained in carbon disulfide with chemical shifts reported as τ in parts per million relative to internal TMS.

goes similar changes and exhibits two signals of unequal intensity at τ 8.03 and 8.06 (Figure 1B). Furthermore, at this temperature (−24°), two new signals appear: a doublet ($J = 9.1$ Hz) at τ 7.37 and a less intense broader doublet ($J = 7.7$ Hz) at τ 8.98 (7-methine protons; *vide infra*). The most reasonable interpretation of these results is that **2** exists as an equilibrating mixture of nonplanar conformers **2a** and **2b**, with one of these conformers in greater concentration.[11] Previous studies of cycloheptatriene systems have shown[1,2,5] that the *syn* or "axial" 7-proton is shielded[2] and therefore occurs upfield (τ 8.83–8.93) in comparison to the *anti-* or "equatorial" 7-proton (τ 6.67–6.99).[4b] From a consideration of the areas in the −24° spectrum of **2** (Figure 1B) and the relative positions of the 7-methine signals, we assign the resonances at τ 7.37, 8.06, and 9.23 to the 7-methine, 1-methyl, and 7-*t*-butyl protons, respectively, of conformer **2a**, and the signals at τ 9.08, 8.03, and 8.94 to the analogous protons of conformer **2b**. The striking conclusion is that **2a**, *the conformer with the "axial" 7-t-butyl group, is more stable.* This result is to be compared with the recent finding[5] that in 7-*t*-butylcycloheptatriene the "equatorial" conformer is more stable.

It should be noted that the chemical shift for the 7-methine proton in **2b** is 0.21 ppm higher than the value reported for 7-*t*-butylcycloheptatriene.[5] Furthermore, in **2b**, $J_{H_6-H_7}$ is somewhat higher than that reported for the analogous vincinal coupling in **1**.[2,5] These observations can be explained by noting that the *t*-butyl–methyl interaction in **2b** might cause the C_1–C_7–C_6 portion of the molecule to depart further than normal from the C_1–C_2–C_5–C_6 plane.[12] The net result would be greater shielding of the axial proton with a concurrent increase in the H–C_6–C_7–H dihedral angle, and hence in $J_{H_6-H_7}$.

The activation energy for the inversion process **2a** ⇄ **2b** was determined by comparing the line shapes of the *t*-butyl absorptions in the experimental spectra with those of theoretical spectra having various values of the mean lifetime (τ).[13,14] From the above treatment and an Arrhenius plot of the rate data, $E_a = 18.9 \pm 1.7$ kcal/mol[15] and $\log A = 15.4 \pm 1.3$, with the rate constant for the ring inversion at the coalescence temperature,[16] $k_{28^\circ\mathrm{C}}$, 58.8 sec^{-1}.

We note further, in a preliminary way, other interesting changes which occur in the spectrum of **2** at lower temperatures. Between approximately −45 to −80° the *t*-butyl resonance at τ 8.94 for the less stable conformer **2b** gradually broadens and then finally sharpens (at −104°) to three singlets of equal intensity at τ 8.78, 8.95, and 9.11 (Figure 1C). We ascribe these resonances to the three magnetically nonequivalent or anisochronous methyl groups in **2b** as depicted in **3**. To our knowledge, this is the first example of the direct nmr observation of three distinct methyl resonances for the *t*-butyl group in an organic molecule.[17] The thermodynamic parameters for these processes along with related studies are in progress and will be reported in further publications.



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[11] We do not believe that the nmr spectral properties of **2** are indicative of a norcardiene. See E. Ciganek, *J. Am. Chem. Soc.*, **87**, 652, 1149 (1965).

[12] L. H. Knox, E. Velarde, and A. D. Cross, *ibid.*, **87**, 3727 (1965).

[13] The theoretical spectra were calculated using a FORTRAN IV coded program based on the equations of Gutowsky and Holm: H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956); for these calculations T_2 was determined from the average of the widths at half-height of the two *t*-butyl peaks under conditions of no exchange.

[14] C. A. Cupas, J. M. Bollinger, and M. Haslanger, *J. Am. Chem. Soc.*, **90**, 5502 (1968), and references therein cited.

[15] Errors reported are for the 90% confidence interval.

[16] T_c, the coalescence temperature, was taken as the temperature at which maximum broadening occurred.

[17] For examples where two signals of a *t*-butyl group are observed see F. A. L. Anet, M. St. Jacques, and G. N. Chmurny, *J. Am. Chem. Soc.*, **90**, 5243 (1968); J. P. N. Brewer, H. Heaney, and B. A. Marples, *Chem. Commun.*, 27 (1967).

[18] National Science Foundation Predoctoral Trainee, 1968–1969.

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The Thermal Rearrangement of *anti*-9-Methyl-*cis*-bicyclo[6.1.0]nonatriene and *syn*-9-Methyl-*cis*-bicyclo[6.1.0]nonatriene

Sir:

The thermolysis of bicyclo[6.1.0]nona-2,4,6-triene at *ca.* 100° leads to a mixture of *cis-* and *trans*-8,9-dihydroindenes in a ratio of 9:1, respectively.[1-4] The stereochemical course of this reaction is not in accord with the prediction made by an orbital symmetry analysis for the concerted electrocyclic reaction.[5,6] Research conducted on the thermolysis of bicyclo[6.1.0]nona-2,4,6-trienes substituted at C_9 has resulted in the formation of substituted 8,9-dihydroindenes,[7,8] the stereochemistry of which provokes interesting questions with regard to the concerted or nonconcerted nature of this reaction.

We wish to report on the study of the thermolysis of *anti*-9-methyl-*cis*-bicyclo[6.1.0]nona-2,4,6-triene (**1**) and *syn*-9-methyl-*cis*-bicyclo[6.1.0]nona-2,4,6-triene[9] (**2**). The results of this study have important bearing on the mechanistic nature of this rearrangement.

The *syn* isomer **2** was readily available from a procedure developed by Katz.[9] The *anti* isomer was prepared from the alcohol[10] **3** by conversion to the tosylate **4** with tosyl chloride and pyridine, followed by reduction of **4** with lithium aluminum hydride to give **1**. The nmr spectrum of **1** was typical of bicyclo[6.1.0]nona-2,4,6-trienes, with the six vinyl protons at τ 4.2 (multiplet), three methyl protons plus two tertiary cyclopropyl protons at τ 7.8 (multiplet), and a tertiary cyclopropyl proton at τ 9.5 (multiplet).

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[1] E. Vogel, *Angew. Chem.*, **73**, 548 (1961).

[2] E. Vogel, W. Wiederman, H. Kiefer, and W. Harrison, *Tetrahedron Letters*, 673 (1963).

[3] E. Vogel, W. Grimme, and E. Dinné, *ibid.*, 391 (1965); see footnote 8.

[4] W. Grimme, *Chem. Ber.*, **100**, 113 (1967).

[5] R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).

[6] H. C. Longuet-Higgens and E. W. Abrahamson, *ibid.*, **87**, 2046 (1965).

[7] K. F. Bangert and V. Boekelheide, *ibid.*, **86**, 905 (1964).

[8] G. J. Fonken and W. Moran, *Chem. Ind.* (London), 1841 (1963).

[9] T. J. Katz and P. J. Garratt, *J. Am. Chem. Soc.*, **86**, 4877 (1964).

[10] D. Phillips, *ibid.*, **77**, 5179 (1955); S. Akiyoshi and T. Matsuda, *ibid.*, **77**, 2476 (1955).