(37%), 18.1 (6% corresponding to the retention time of authentic *trans*-**5**), and 24.0 min. (5%).

B.—To 0.2 ml. (1.3 equiv.) of sodium methylsulfinyl carbanion in dimethyl sulfoxide[13] was added 21 mg. of **1**(OTs). After 1 hr. at room temperature the mixture was worked up, giving 10 mg. (106%) of a colorless oil: $\lambda_{\max}^{\mathrm{CCl_4}}$ 2.8 (w), 5.77 (vw), 5.85 (w), 7.3, and 8.5 μ (w). Thin layer chromatography on silica gel (chloroform) showed one large spot at R_f 0.20 (same as $\Delta^{1(9)}$-10-octalol) and small spots at R_f 0.15, 0.26, 0.34, and 0.74.

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[13] E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 866 (1962).

The Conformational Free-Energy Difference of the Nitro Group

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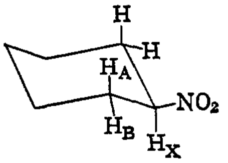
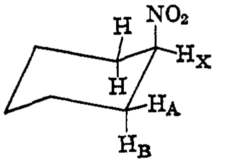
Received June 8, 1965

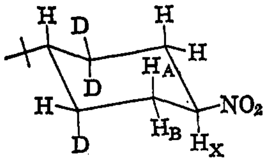
In a recent communication[2] Feltkamp and Franklin have reported an approximate value of 1 kcal./mole for the conformational free-energy difference of the nitro group and that nitrocyclohexane therefore exists approximately 85% in conformer I at 26°. A previous report[3] had suggested that at 26° in 10% w./v. solution in carbon tetrachloride, nitrocyclohexane exists exclusively in conformer I. Feltkamp and Franklin have calculated their values by their published method[4] (a method similar to that reported by Garbisch[5] for measuring the equilibrium constants of mobile six-membered ring systems) from the band widths of the n.m.r. multiplets of the X proton of nitrocyclohexane and of *trans*-4-*t*-butylnitrocyclohexane obtained from the literature, and approximated for *cis*-4-*t*-butylnitrocyclohexane. No mention is made of solvent.[6]



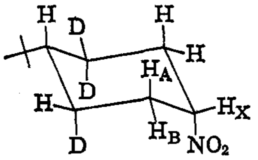
I



II



III



IV

In continuing our n.m.r. study of nitrocyclohexanes[7-9] we have now measured the conformational preference of the nitro group in nitrocyclohexane neat, in 33 and 50 mole % in deuterated chloroform, and in 20 and 33 mole % in acetone and in acetonitrile at 37° by the signal-width method,[4,5] using the partially deuterated compounds *trans*- and *cis*-4-*t*-butylnitrocyclohexane-3-(axial),5,5-d_3 (III and IV, respectively) for conformationally homogeneous models. The deuterated compounds give simplified spectra which afford more accurate measurements of coupling constants and signal band widths. No appreciable difference was found in the conformational preference of nitrocyclohexane in the pure state and in the two dilutions in deuterated chloroform at 37°. Under these conditions a value of 78 ± 4% of conformer I ($K = 3.5 \pm 0.5$) was found, and a conformational free-energy difference (ΔG) of 0.78 ± 0.10 kcal./mole was obtained for the nitro group. No appreciable difference was found in acetone and acetonitrile or between the two concentrations used in each solvent. In these solvents 79.5% of conformer I was obtained by using the signal band width of III and IV measured in deuterated chloroform as reference. The measurements were made from average band-width values obtained from at least four spectra in each dilution in each solvent. The reproducibility of measurements of band widths was about ±0.2 c.p.s.

Using the notation of Garbisch[5] the band width of the X proton equals $2J_{\mathrm{I}} = 2(J_{\mathrm{AX}} + J_{\mathrm{BX}})$ in III; $2J_{\mathrm{II}} = 2(J_{\mathrm{AX}} + J_{\mathrm{BX}})$ in IV; and $2J° = 2(N_{\mathrm{I}}J_{\mathrm{aa}} + N_{\mathrm{II}}J_{\mathrm{ee}} + N_{\mathrm{I}}J_{\mathrm{ea}} + N_{\mathrm{II}}J_{\mathrm{ae}})$ in the mobile nitrocyclohexane, where N_{I} and N_{II} are mole fractions of conformers I and II, respectively.

$$N_{\mathrm{I}} = \frac{J° - J_{\mathrm{II}}}{J_{\mathrm{I}} - J_{\mathrm{II}}} \qquad K = \frac{J° - J_{\mathrm{II}}}{J_{\mathrm{I}} - J°}$$

The spectra were determined at 60 Mc. at 37° with a Varian A-60 spectrometer. The spectrum of III in deuterated chloroform gave ν_{X} = 259 c.p.s., $2J_{\mathrm{I}}$ = 31.6 c.p.s., J_{aa} = 11.6, and J_{ea} = 4.2 c.p.s. Our reported values for J_{aa} and J_{ae} obtained from the nondeuterated compound[7] were 11.3 and 4.2 c.p.s. The spectrum of IV gave ν_{X} = 270.5 c.p.s. and $2J_{\mathrm{II}}$ = 13.5 c.p.s. Accurate values of J_{ae} and J_{ee} could not be obtained from the spectrum of IV, but they are not equal. The spectrum of nitrocyclohexane neat, as well as in the two dilutions in deuterated chloroform, gave ν_{X} = 263 c.p.s. and a signal band width $2J°$ = 27.6 c.p.s. The chemical shifts of the X protons are too close for reliable calculation of ΔG by the chemical shift method of Eliel.[10]

The deuterated compounds II and IV were obtained from the trideuterated 4-*t*-butylcyclohexanone-3(axial),-5,5-d_3 by the method reported for the corresponding nondeuterated compounds.[7] The trideuterated ketone was obtained by iodine-catalyzed dehydration of a mixture of *cis* and *trans* isomers of 4-*t*-butyl-4-hydroxycyclohexanol-3,3,5,5-d_4[11] followed by platinum-catalyzed hydrogenation of the trideuterated alkene and subsequent chromic acid oxidation of the secondary alcohol by the method of Brown and Garg.[12]

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[1] Public Health Service Predoctoral Fellow, Fellowship No. 5-F1-GM-18,507-03.

[2] H. Feltkamp and N. C. Franklin, *J. Am. Chem. Soc.*, **87**, 1616 (1965).

[3] W. Hofman, L. Stefaniak, T. Urbanshi, and M. Witanowski, *ibid.*, **86**, 554 (1964).

[4] H. Feltkamp and N. C. Franklin, *Ann. Chem.*, **683**, 55 (1965).

[5] E. W. Garbisch, Jr., *J. Am. Chem. Soc.*, **86**, 1780 (1964).

[6] Variations of ΔG in different solvents is a possibility.

[7] A. C. Huitric and W. F. Trager, *J. Org. Chem.*, **27**, 1926 (1962).

[8] W. F. Trager, F. F. Vincenzi, and A. C. Huitric, *ibid.*, **27**, 3006 (1962).

[9] A. C. Huitric, J. B. Carr, W. F. Trager, and B. J. Nist, *Tetrahedron*, **19**, 2145 (1963).

[10] E. L. Eliel, *Chem. Ind.* (London), 568 (1959).

[11] W. F. Trager, B. J. Nist, and A. C. Huitric, *Tetrahedron Letters*, 267 (1965).

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