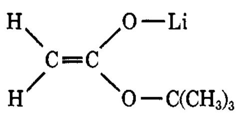

I

ppm. The infrared spectrum (fluorolube) possesses a band at 1620 cm^{-1}, assigned to the carbon double bond stretch, and has no band in the region from 1675 to 2000 cm^{-1}.

The following procedure describes the preparation of lithio *tert*-butyl acetate. A dry 2-l. round-bottomed flask, equipped with mechanical stirring and mercury relief valve, is flushed with nitrogen and immersed in an ice–water bath. The flask is charged with 1 mol of *n*-butyllithium dissolved in 1.5 l. of hexane and 1 mol (101 g) of diisopropylamine is added over a period of 10 min. The flask is then immersed in a Dry Ice–acetone bath and 1 mol (116 g) of *tert*-butyl acetate is added over a 15-min period. The reaction mixture is stirred an additional 30 min at −78° and then allowed to reach room temperature. Solvent and amine are stripped off with a rotary evaporator. Any yellow color in the solid may be removed by trituration with hexane. The weight of lithio *tert*-butyl acetate obtained is 116 g (95%). Addition of samples to water followed by glpc analysis for *tert*-butyl acetate indicates a purity greater than 98%.

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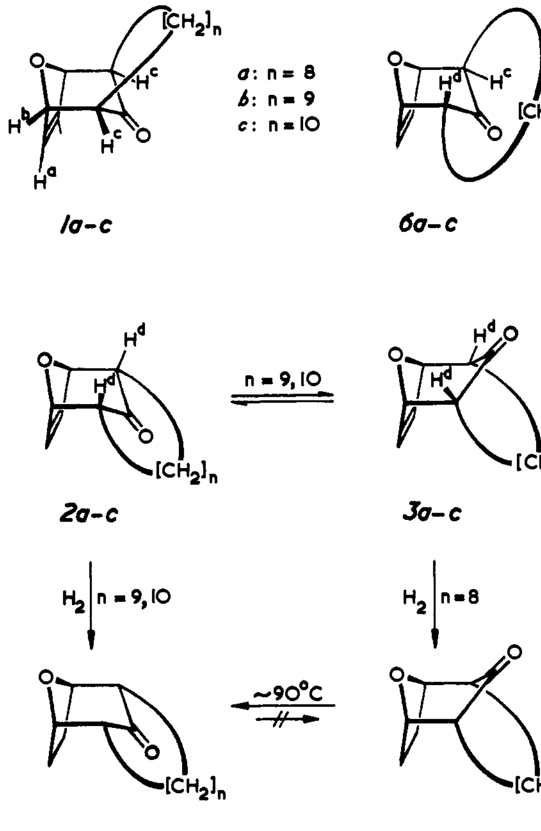
Direct Observation of Chair–Boat Equilibria in Bridged Six-Membered Rings

Sir:

Of the various conformers of saturated six-membered rings the chair is generally by far the most stable.[1] If nonchair populations play some role it is normally the twist form which takes a part, although some of the spectroscopic evidence has been regarded to be still tenuous.[1h] The true, classical boat arrangement usually does not have a finite lifetime, but serves as a transition state for pseudorotation[2] of the twist conformer.

We wish to report the first examples of chair–boat equilibria which exclude the twist conformer and can be frozen out on the nmr time scale. Debromination of 2,12-dibromocyclododecanone[3] with a dry, acid-free zinc–copper couple in the presence of furan[4] yielded two distinct crystalline forms of cycloadducts[5] which after slow (*ca.* 2 days at 25°) crystallization from isooctane could be separated manually. 16-Oxatricyclo[11.2.1.1^{2,12}]heptadec-14-en-17-one of mp 130° was the minor isomer **1b**: nmr (TMS, CCl$_4$) δ a 6.16 (2 H, s), b 4.62 (2 H, s), c 2.16 ppm (2 H, complex); ir (CCl$_4$) ν_{CO} 1703 cm^{-1}; dipole moment 1.7 D.[6]



1a–c **6a–c** **2a–c** **3a–c** **4a–c** **5a**

The nmr spectrum of the major isomer, mp 85°, was temperature dependent (*cf.* Figure 1) and at 0° in CCl$_4$ solution two individual conformers **2b** and **3b** were clearly discernible:[7] nmr (TMS, CCl$_4$) of **2b**, a 6.15 (2 H, s), b 4.76 (2 H, d, J = 3.5 Hz), d 3.32 (2 H, complex); **3b**, a 6.42 (2 H, s), b 4.88 (2 H, d, J = 7.5 Hz), d 2.78 ppm (2 H, complex); dipole moment of **2b** and **3b** 2.4 D; ir (CCl$_4$) 1704 and 1714 cm^{-1}; interestingly in the mull only one band at 1713 cm^{-1} was visible, indicative of the chair conformer **2b**. Further separation of the filtrate yielded **6b**: nmr a 6.12 (2 H, major quartet and two pairs of symmetrical satellites), b 4.56 (2 H, complex), c 2.10 (1 H, complex), d 3.28 (1 H complex); ir (CCl$_4$) ν_{CO} 1713 cm^{-1}.

The assignment of six-membered chair to **1b**, **2b**, and **6b** and of boat to **3b** rests on dipole moment measurements and on nmr comparison with model bicyclic[4] as well as conformationally rigid tricyclic compounds in which the aliphatic chain is shortened to four methylene groups (**1** and **3**, n = 4). Furthermore, the equilibrium

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(1) (a) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York, N. Y., 1965; (b) M. Hanack, "Conformation Theory," Academic Press, New York, N. Y., 1965; (c) F. G. Riddell, *Quart. Rev., Chem. Soc.*, **21**, 364 (1967); (d) C. Romers, C. Altona, H. R. Buys, and E. Havinga, *Top. Stereochem.*, 4, 39 (1969); (e) J. B. Lambert, *Accounts Chem. Res.*, **4**, 87 (1971); (f) E. L. Eliel, *Angew. Chem., Int. Ed. Engl.*, **11**, 739 (1972); (g) J. E. Anderson, *Fortschr. Chem. Forsch.*, in press; (h) G. M. Kellie and F. G. Riddell, *Top. Stereochem.*, in press.

(2) J. B. Hendrickson, *J. Amer. Chem. Soc.*, **89**, 7047 (1967).

(3) E. W. Garbisch and J. Wohllebe, *J. Org. Chem.*, **33**, 2157 (1968); *Chem. Commun.*, 306 (1968).

(4) H. M. R. Hoffmann, K. E. Clemens, and R. H. Smithers, *J. Amer. Chem. Soc.*, **94**, 3940 (1972); see also H. M. R. Hoffmann, D. R. Joy, and A. K. Suter, *J. Chem. Soc. B*, 57 (1968), and intervening papers.

(5) Elemental analyses and mass spectra were consistent with the structures assigned; the methylene protons of the tricyclics appear uniformly as a broad peak at δ 1.3 ppm in the nmr spectrum.

(6) All dipole moments were determined in solvent benzene; the probable error is ±0.2 D.

(7) For the ketonization of strained meta-bridged *p*-nitrophenols see V. Prelog, *et al.*, *Helv. Chem. Acta*, **30**, 1465 (1947); **31**, 1325 (1948); **33**, 356 (1950). See also D. J. Cram and J. M. Cram, *Accounts Chem. Res.*, **4**, 204 (1971); F. Vögtle, P. Neumann, and M. Zuber, *Chem. Ber.*, **105**, 2955 (1972), and references therein.

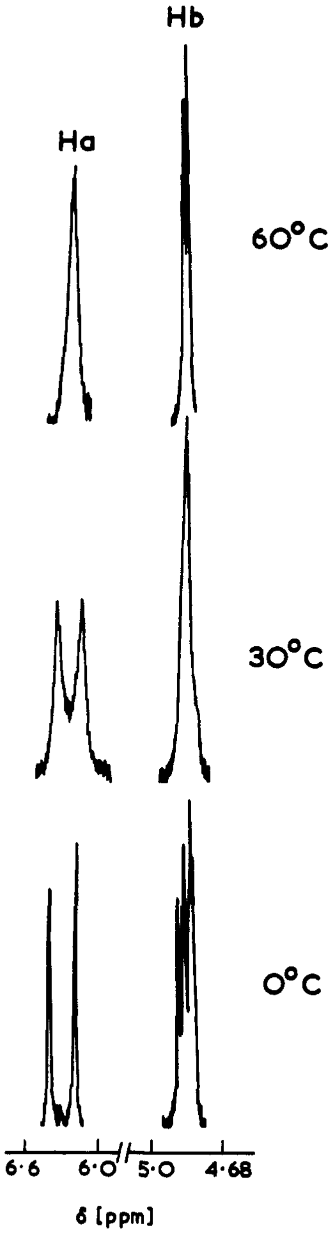

Figure 1. Temperature-dependent nmr of $2b \rightleftharpoons 3b$ in CCl_4.

$2b \rightleftharpoons 3b$ was found to be solvent dependent, **2b** being favored by 40 cal/mol in CCl_4, while the boat conformer **3b** was stabilized by 600 cal/mol in more polar solvents such as $(CD_3)_2CO$ and $CDCl_3$.

A complete nmr line-shape analysis[8] of the olefinic resonance of the mobile system $2b \rightleftharpoons 3b$ in CCl_4 and in $(CD_3)_2CO$ over the temperature range of full resolution to coalescence (-5 to $+60°$) revealed an energy of activation $\Delta G^{\ddagger} = 16.0$ and 16.4 kcal/mol ($\pm 2\%$), corresponding to $\Delta H^{\ddagger} = 16.7$ kcal/mol and $\Delta S^{\ddagger} = 1.5$ eu ($\pm 50\%$), respectively. The Arrhenius parameters in CCl_4 were $E_a = 17.3$ kcal/mol and log $A = 13.7$.

Reduction of **2b** + **3b** with hydrogen over Adams' catalyst gave 16-oxatricyclo[11.2.1.1^{2,12}]heptadecan-17-one (**4b**): mp 95°; nmr *inter alia* b 4.36 (2 H, complex), d 3.16 (2 H, complex); ir 1713 cm^{-1}; dipole moment 1.5 D. In this instance the nmr spectrum showed no pronounced change with temperature and it is clear that the six-membered ring in **4b** has lost its mobility and formed a stable chair which is bridged diequatorially by the methylene chain.

2,13-Dibromocyclotridecanone[9] reacted with furan in the presence of zinc–copper couple to give the mobile homotricyclic pair $2c \rightleftharpoons 3c$. Interestingly, the nmr spectrum could no longer be resolved on going down to $-80°$; on further cooling the compound crystallized from solvent $CFCl_3$. Thus, the activation barrier must be lower than 8 kcal/mol in this case. In solvent CCl_4 the chair conformer **2c** was estimated to be more stable than **3c** by 650 cal/mol, but by only 380 cal/mol in $(CD_3)_2CO$ and $CHCl_3$.[10] Both the diaxially substituted chair **1c** and the skew isomer **6c** were also formed in the reaction.

Finally, cycloaddition of 2,11-dibromocycloundecanone[3] to furan yielded the diaxially bridged nortricycle 3a, which was frozen as a boat and did not flip to 2a below 140°, *i.e.*, $\Delta G^{\ddagger} > 22$ kcal/mol. On reduction of the double bond the boat conformation was retained (*cf.* **5a**), but on heating to *ca.* 90° the diequatorially bridged chair **4a** was formed quantitatively and as far as we can tell, irreversibly, since further heating up to 160° did not regenerate the boat derivative **5a**.

In conclusion the series of tricyclic model compounds **2b–c** and **3a–c** seem unique in that they can adopt truly symmetrical boat conformations. Where chair–boat interconversion is possible, the transition state is presumably close to a symmetrical half-boat with five carbon atoms in one plane and involving only small entropy changes.

The reactions described are of synthetic interest as a new annelation procedure and they also yield insight into the geometry of the intermediate allyl cation as well as the ensuing transition state, as we shall discuss in the full paper.

Acknowledgments. We thank Dr. J. E. Anderson for discussions, Professor H. Hellmann of Chemische Werke Hüls for a generous sample of cyclododecanone, Dr. B. Willhalm of Firmenich & Cie, Geneva, for mass spectrometric analyses, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

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[8] I. O. Sutherland, *Annu. Rep. NMR (Nucl. Magn. Resonance) Spectrosc.*, **4**, 71 (1971).

[9] Prepared from cyclotridecanone and bromine (2 mol equiv) in ether at 0°. Only the high melting isomer, mp 110°, was used.

[10] It is assumed that the vicinal coupling constant of the bridgehead protons is 3.5 Hz in **2c** and 7.5 Hz in **3c**, as observed for **3a** as well as **2b** and **3b**. As chemical shifts coalesce the coupling constants average to the weighted mean of the individual conformers. At 25° in CCl_4 solution the observed coupling constant of the mobile tricyclic was 5.5 Hz (**2c**:**3c** = 3:1) and in $(CD_3)_2CO$ and $CDCl_3$ 6.0 Hz (**2c**:**3c** = 1.9:1). The experimental error of this estimate is probably not greater than ±15%.

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Synthesis and Reactions of Some New Aryldiazo Complexes of Iridium

Sir:

We wish to report a facile synthetic route to a variety of new iridium aryldiazo complexes and to present preliminary information on their characterization. The