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SUBSTITUTED 1,2-DIMETHYL-2-NORBORNYL CATIONS

UNEQUIVOCAL PHYSICAL EVIDENCE FOR EQUILIBRATING STRUCTURES

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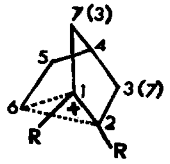
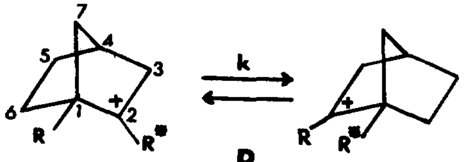
The direct observation (and solvolyses studies[1]) of symmetrically 1,2-disubstituted norbornyl cations has attracted obvious attention because of the clearcut structural distinction which can, in theory, be made between a symmetrical structure A and equilibrating structure B. Previous workers[2,3] have shown that where R = p-anisyl or methoxy, the n.m.r. evidence clearly shows B, since k can be made slow on the n.m.r. exchange time scale by choosing a suitable temperature. With R = methyl, this is not the case; even at -130°, only <u>one</u> methyl peak (6H) is observed.[4,5] Olah *et al*[4] have used C^{13}, H^1 n.m.r. and Raman spectroscopy to obtain evidence favouring B but the procedures used are subject to controversy (i.e. comparisons of observed chemical shifts to those expected of various "models"). This communication reports an alternative procedure which shows unequivocally that the B situation exists.

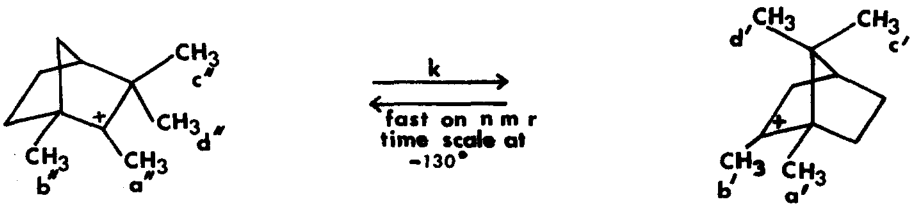


A



B

The addition of two <u>further</u> geminal methyls to A or B at C3/C7 is extremely unlikely to change the basic cation structure and in agreement, we have not been able to "freeze out" in the n.m.r. spectrum the individual isomers I and II (assuming their existence) at -130°. The



II I

evidence for equilibrating structures is based on: (1) the structures I and II are now non-degenerate and happen not to be isoenergetic ($\Delta G \neq 0$, $K \neq 1$), so that the averaged a and b methyl peaks from I and II have different chemical shifts; and (2) these averaged chemical shifts, befitting an equilibrium situation, are temperature dependent.

Thus, addition of the alkene IV or the cyclopropane V[6] to FSO_3H-SO_2ClF (1:4) at -130° results in a colourless solution whose partial n.m.r. spectrum at -122.5° is shown schematically in Fig. 1. The noteworthy feature is the presence of four separate methyl peaks, labelled W, X, Y and Z, from low to high field. The protonation of IV or V leads logically to I and/or II and various aspects of the n.m.r. spectrum are consistent with this.[7] Since methyl groups closest to the positive charge are most deshielded, a and b (structures I and II) = W and X (or X and W). Since b should experience residual coupling with C3 protons,[8] given a reasonable population of I, we have assigned the marginally wider of the two, W, to b. This assignment means isomer I is dominant[9] but the opposite assignment would in no way affect the basic conclusions.

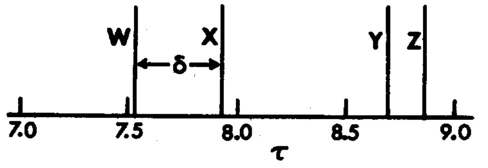
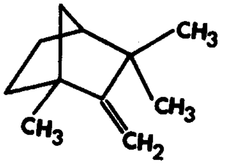
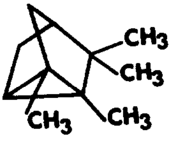


Fig. 1 - Schematic spectrum of I-II at -122.5°
showing only the four methyl peaks



IV



V

Numerical Evaluation of K and ΔG for II ⇄ I (assuming $\Delta S = 0$, $\Delta G \sim \Delta H$)

The assumptions necessary in this evaluation do not affect the basic conclusions, stated earlier, regarding the evidence that an equilibrium is present. The separation δ_{WX} (Fig. 1) was directly measured at 16 temperatures from -46.6 to -122.5°.[10] In addition, the chemical shifts of W and X were measured relative to internal tetramethylammonium cation reference. A plot of the temperature dependence of both peaks is shown in Fig. 2.

Certain complications[11] account for the sharp break in the symmetrical convergence of W and X and even though δ_{WX} steadily decreases over the complete temperature range, one cannot use the δ_{WX} data above -90°. In applying the equation $I/II = e^{\frac{-\Delta G}{RT}}$, it is necessary to have an understanding of the chemical shifts of the individual cations I and II. In this work, the chemical shifts expected in I or II are set up to generate a variable parameter ω (Fig. 3) and

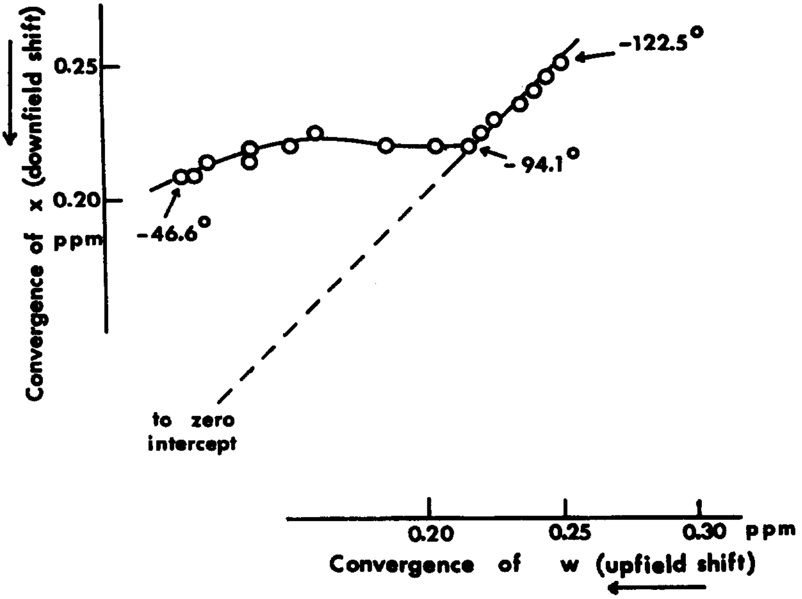


Fig. 2 - Convergence Behaviour of W and X

this was then varied by computer in the distribution equation in an attempt to obtain a best fit.[13] Two fitness criteria can be used: (a) the least squares correlation coefficient R can be maximised for ω variation, and (b) the intercept of $\ln \frac{\omega-\delta}{\omega+\delta}$ vs. $1/T$ should be zero. In practice, the two did not coincide, although R does not vary greatly, and we have chosen the zero intercept data as a more "real" criterion. From three separate results, $\Delta G = 335 \pm 100$ calories/mole (K ca. 1.7 at 25°, 3.1 at -123°) and $\omega = 0.9 - 1.2$ p.p.m. Other evidence supports an ω value of this magnitude[14] and lends self-consistency to the results. Thus, we feel that the presence of equilibrating structures is unequivocally established.

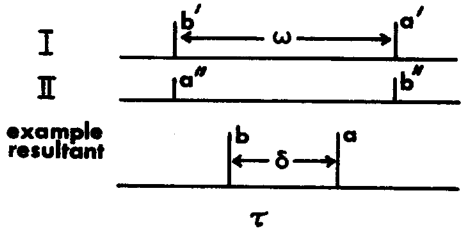
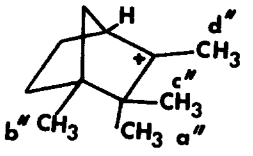


Fig. III - Assumption: that b' in I and a" in II have the same chemical shift and that a' in I and b" in II also have the same chemical shift. In this case I/II = $\frac{\omega-\delta}{\omega+\delta}$.

Acknowledgement. The authors thank the National Research Council of Canada for generous financial support.

References and Footnotes

1. For a recent example, H.L. Goering and J.V. Clevenger, J. Amer. Chem. Soc. **94**, 1010 (1972).
2. P. von R. Schleyer, D.C. Kleinfelder and H.G. Richey,Jr., Ibid **85**, 479 (1963).
3. A. Nickon and Y.-i Lin, Ibid **91**, 6861 (1969).
4. G.A. Olah, J.R. DeMember, C.Y. Lui and R.D. Porter, Ibid **93**, 1442 (1971).
5. K. Ranganayakulu, unpublished results.
6. 2-Methylfenchol underwent spontaneous dehydration on heating and the two major products IV and V were isolated by preparative g.l.c. See also J. Wolinsky, D.R. Dimmel and T.W. Gibson, J. Org. Chem. **32**, 2087 (1967).
7. No peaks below τ 6.8, as expected. A peak at τ 7.34 can be assigned to the C4 proton.
8. From other examples studied in this laboratory, $J_{2CH_3\text{-}3H} = 1.5 - 2$ Hz.
9. Unpublished work using 1,2-dimethyl-2-norbornyl cations with a single methyl at C3 shows that for an *endo*-methyl (or *anti*) both isomers are of virtually equal energy but with an *exo*-methyl (or *syn*), the *syn* position is definitely preferred. Hence the presence of both *endo* or *anti* and *exo* or *syn* methyls should still favour the *anti-syn* isomer.
10. The data (chemical shifts of W, X, Y, Z, δ_{WX}, and half-widths at half-height) can be obtained from the authors; temperature variation $\pm 0.1^{\circ}$, error in δ_{WX} ca. 0.002 p.p.m. Above -45°, the ions I, II, III are converted rapidly to other products.
11. A third isomer III, present in ca. 2-3% total, is a component of the equilibrium below -90°, but is not a contributor to the averaged peaks shown in Fig. 1. The peaks of III are not themselves visible. Above -80°, the *exo*-3,2-methyl shift[12] interconverting II and III becomes rapid on the n.m.r. time scale so that the four peaks in Fig. 1 are now the average of all three cations. An unequal line broadening reaches a maximum at about -85° (Y > W > X with Z remaining unchanged) in accord with expectations for the change in a major population peak based on standard n.m.r. line broadening theory. The unequal broadening occurs because of variable chemical shift differences of the coalescing peaks; expected d > b > a with c unchanged, assuming III has chemical shifts similar to the camphenehydro cation and others.[12] The presence of III can be shown mathematically to cause the erratic behaviour shown in Fig. 2 but it at least allows one to definitively assign d = Y, c = Z in cations I and II.



III

12. E. Huang, K. Ranganayakulu and T.S. Sorensen, J. Amer. Chem. Soc. **94**, 1780 (1972).
13. Slightly more complex variations were also used, in which an additional parameter was introduced. However, the paucity of data points makes this a questionable procedure.
14. In other cations (similar to I and II) where we believe that the equilibrium overwhelmingly favours one of the isomers, values of $\omega \sim \delta$, in this range, are observed.