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CONFORMATIONAL INTERCONVERSION IN A STRAINED KETONE: TETRA-t-BUTYLACETONE. A DNMR (^{1}H, ^{13}C) STUDY.

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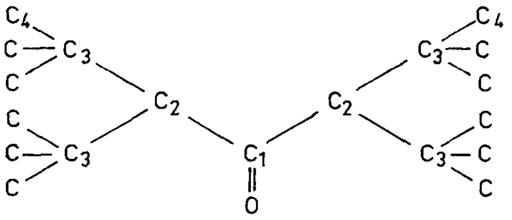
Conformational preferences of branched aliphatic alkyl ketones have been recently approached by topological or topographical correlations of spectroscopic data.[1] However, up to date, very little is known about the barriers to rotation around the sp^2 (carbonyl)-sp^3 (α carbon) C-C bonds in these compounds, as opposed to the well-documented results concerning rotations about C sp^2-C sp^3 bonds in aromatic or poly-heteroatomic systems.[2]

We report here preliminary results about conformational interconversion in a strained ketone: tetra-t-butylacetone (I). To our knowledge, it is the first observation of this type, by DNMR, for aliphatic alkyl ketones. Recent publications show evidence for restricted rotations in tetraisopropylethylene[3] and some barrier heights have been measured in three crowded 1,1 disubstituted alkenes.[4] However, the authors cite the failure to observe, by NMR, slow rotations in closely related ketones (R-CO-CMe$_2$tBu with R=H, Me or CH$_2$Br).[4a]

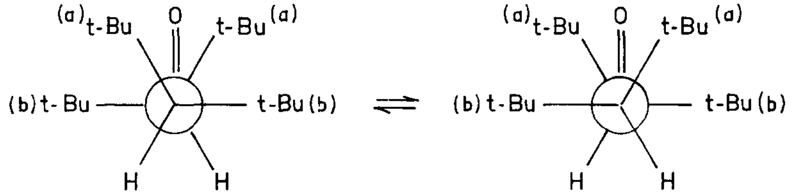
In this field, tetra-t-butylacetone is an attractive probe since, it can be hoped that the crowding of alkyl groups, which creates major distortions of standard geometrical parameters (as shown by crystallographic data[5]) might severely restrict the rotations of alkyl radicals down to a rate in the range of dynamic NMR.

(I)



At room temperature (294°K) in CDCl$_3$ the ^{1}H spectrum of (I) consists of two peaks of equal intensity for the t-Bu protons (doublet centered at δ = 1.15 ppm, $\Delta\delta$ = 0.053 ppm) and only one narrow signal for the hydrogens linked to C$_2$ (2.77 ppm). The ^{13}C spectrum exhibits single peaks for the carbonyl carbon C$_1$ and the α carbons C$_2$ (at 217.3 and 70.0 ppm downfield from TMS) whereas the signals corresponding to C$_3$ and C$_4$ are split into equal doublets, centered at 36.6 ppm ($\Delta\delta$ = 0.29 ppm) for C$_3$ and 32.9 ($\Delta\delta$ = 0.33) for C$_4$. These data are quite consistent with strain energy calculations[6] and crystallographic data[5] which indicate that, to minimize steric interactions, the molecule prefers conformations with a t-Bu group nearly perpendicular to the C-CO-C plane for each alkyl radical, and with a two-fold symmetry axis passing through the carbonyl. This results in a two-by-two equivalence of the t-Bu groups of the two radicals, within two non-equivalent sets (denoted by a and b in Fig. II).[7] The two corresponding equivalent conformations may be interconverted by rotations about the C_1-C_2 bonds. However, the magnetic non-equivalence observed indicates that rotations are slow at room temperature, in the DNMR time scale.

(II)



Temperature dependence of the spectra has been analyzed by ^{1}H NMR. As the temperature rises, the t-Bu doublet (whose separation is 3.5 Hz, at 60 MHz, at low temperature) coalesces at 314°K and then gives a narrowing peak.[8] Line shape analysis (for an uncoupled two site exchange) leads to a free energy of activation of $\Delta G^{\ddagger} = 17.3$ Kcal. mole^{-1} at coalescence temperature.[9] This value is confirmed by ^{13}C NMR: coalescence of the doublet corresponding to C_4 signals ($\Delta\delta = 8.5$ Hz at 25 MHz at low temperature) is observed at 326°K.

At this stage, it cannot be ascertained what type of internal deformation (synchronous "windshield wiper" movement or others) really occurs in this interconversion. Work is under way to examine what threshold of steric crowding is necessary to induce, in aliphatic ketones, barriers in the range of dynamic NMR; and to relate them - via conformational maps - to the microscopic internal motions occurring in the interconversion processes.

REFERENCES AND NOTES

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3. R.F. Langler and T.T. Tidwell, Tetrahedron Lett., 777 (1975); D.S. Bomse and T.H. Morton, ibid. 781 (1975).
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5. G. Lepicard, J. Berthou, J. Delettre, A. Laurent and J.P. Mornon, C.R.Acad.Sci. Ser.C, 276, 575 (1973). (The $C_3C_2C_3$ angles are opened up to 118° and the C_2C_3 bonds lengthened to 1.60 Å)
6. J.E. Dubois et al. (to be published).
7. The alternate possibility (consistent with NMR data) of a symmetry plane bisecting the C-CO-C angle seems highly doubtful, as it would lead to strong repulsions between the t-Bu groups of the two radicals.
8. In the temperature range investigated (324 to 233°K) internal rotation of the methyl groups (inside the t-Bu groups) remains fast since no additional splitting appears.
9. Simulation of the spectra has been performed using a program derived from DNMR III: G. Binsch, J.Am.Chem.Soc., 91, 1304 (1969).

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