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BARRIERS TO ROTATION ABOUT sp^3--sp^2 BONDS

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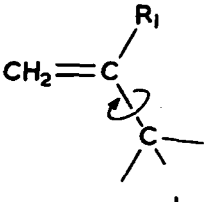

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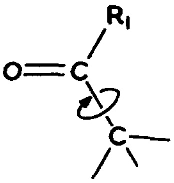

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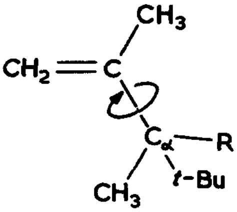
While there have been many recent reports of nmr studies of barriers to rotation about sp$_3$-carbon to sp$_3$-carbon bonds[1], and about phenyl to sp$_3$-carbon bonds[2], much less is known about other sp$_2$-carbon to sp$_3$-carbon bonds such as those in olefins 1 and ketones 2. Recently there appeared simultaneous reports[3,4] on the rotation of an isopropyl group in tetra-isopropyl ethylene, but other than this we know of only one nmr measurement of a barrier, that in the compound 3a, where Bartlett and Tidwell[5] reported a barrier to rotation of about 15 kcal mol^{-1}. We felt that 3a might form the basis for a systematic study of sp3--sp2 barriers.

Table 1 shows the barrier to rotation in the compounds 3a to 3c as measured by complete lineshape treatment of the signal of the methyl group attached to the double bond. This appears as an unequal doublet (each member of which is further split by coupling) below the coalescence



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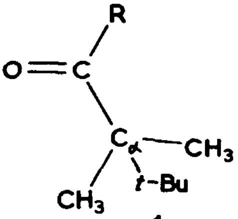
a) R = *t*-Bu
b) *i*-Pr
c) Et
d) Me
e) H
f) CH$_2$Br



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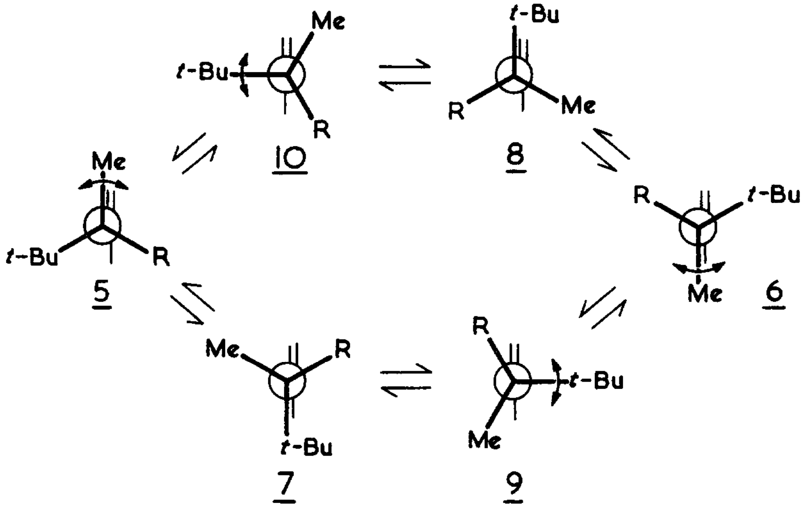
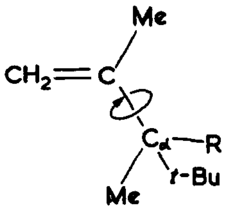


temperature shown, and as a single absorption at higher temperatures. Other signals show the expected changes in agreement with this[6]. Populations and energy differences of conformations are also in the Table.

Significantly, we also examined nmr spectra of 3d, 4d, 4e, and 4f but failed to observe spectral changes with temperature which could be associated with sp^3--sp^2 bond rotation.

Rotation through 360° about the bond shown in a molecule such as 3, produces no conformations which are identical. The nmr results show however that there are two conformations or sets of conformations of comparable energy for 3a, 3b, and 3c. Bartlett and Tidwell have suggested[5] for 3a that these are with the double bond either *cis* to the methyl group 5 or *trans* 6, or more likely, each form is an equilibrium among several metastable conformations close to 5 and 6. The barrier for 3a probably represents the excess energy of whichever of 7 or 8 is the *higher* in energy, for when R = *t*-Bu, interconversion of 5 and 6 requires passage through both 7 and the mirror image of 8 or through 8 and the mirror image of 7.

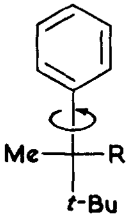
Barriers and Conformer Populations in 3.[a]

	Olefin Rotation		Proportions[c] of the two rotational isomers at low temperature T_L		
	Barrier[b]. $\Delta G^{\#}$	T_c (^oK)	T_L	$p_A : p_B$	$\Delta G_o^{T_L}$
3a R = t-butyl	**15·4**	306	175	42:58	0.11
3b R = i-propyl	**11·2**	214	177	81:19	-0.35
3c R = ethyl	**9·1**	169	142	34:66	0.19

a) ΔG values in kcal/mol. Temperatures in ^oK
b) Near the Coalescence Temperature T_c.
c) p_A refers to downfield of two signals; assignment to conformations is uncertain.

In contrast for 3b and 3c which are less symmetrical, forms closer to 9 and 10 with the t-butyl group as far as possible from the plane of the olefin may be more likely.[7] Now the barrier represents whichever of 7 or 8 is of lower energy since passage through this low energy form makes all other conformations accessible. This contrast satisfactorily explains the difference in barrier between 3a and 3b.

That 3c has a barrier even lower than 3b indicates that as in the substituted toluenes 11, R has a role to play[2b,8] i.e. the interactions of the t-butyl group are not the sole determining feature. The explanation we offered before[8] can apply viz. the angle R--C--t-butyl is greater than 120° due to mutual repulsion, so that in 7 compared with 5 say R is closer to the plane of the olefin, and thus interacts more strongly with it.



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An alternative explanation might lie in slightly different ground-state conformations and interactions as R varies, or it could be that to reduce interactions during the sp^3-sp^2 rotation, secondary rotations about the R--C or the t-butyl--C bonds take place. The energy involved in these secondary rotations may vary be several kcal mol^{-1} as R varies.[1a]

Our inability to observe spectral changes which could be associated with slow rotation in 3d, 4d, 4e and 4f may either mean barriers to such rotation of less than about 6 kcal mol^{-1} or that there is one set of conformations putatively like 5 or 6 which is much more stable than all others.

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2. Leading references in a) B.Nilsson, P.Martinson, K.Olsson, and R.E.Carter, J.Amer.Chem.Soc., (1974), 96, 3190 for compounds with o-substituents; b) J.M.A.Baas, J.M.Van der Toorn, and B.M.Wepster, Recueil, (1974), 93, 133 for compounds without o-substituents.

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6. In addition at even lower temperatures, the t-butyl signals split to 1:1:1 triplets indicating that rotation of that group is slow. These are examples of the well-characterised sp^3-sp^3 rotation.[1a] Barriers to this rotation are 3a) 10.6 and 9.9 kcal/mol, different in the two isomers! 3b) approximately 9.8 kcal/mol in both isomers. 3c) not observed.

7. A pair such as 6 and 9 correspond to parallel and perpendicular conformations of α-substituted toluenes. The effect of substituents in the latter case have been discussed in some detail in J.E.Anderson and H.Pearson, J.Chem.Soc.Perkin II, (1974), 1779.

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