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THE DYNAMICS OF CARBON-CARBON SINGLE BOND ROTATION IN ACYCLIC ALCOHOLS

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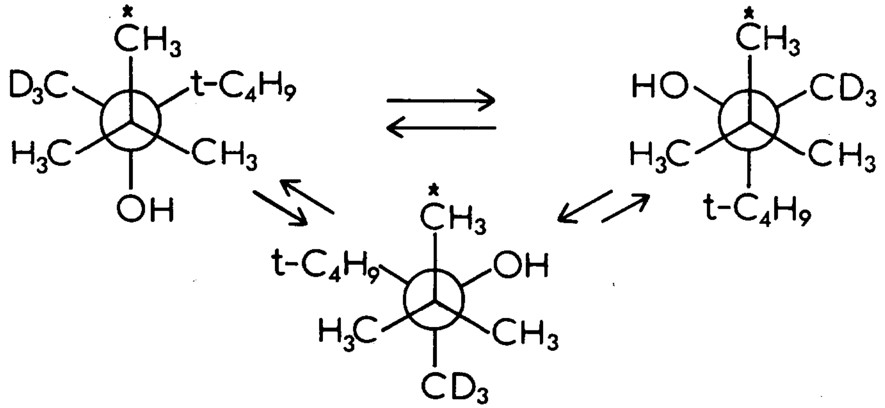
Although there is an increasing amount of data regarding rotation about carbon-carbon,[2a-d] carbon-nitrogen,[2e] and carbon-phosphorus[2f] single bonds, there exists a dearth of information concerning the effect of hydroxyl on the dynamics of carbon-carbon single bond rotation.

Examination of the ^1H dnmr spectrum (60 MHz) of $(t\text{-}C_4H_9)_2(CD_3)COH$ (4% in CH_2CHCl; Figure) at -37.1° revealed a sharp singlet resonance due to tert-butyl (δ1.045) consistent with rapid tert-butyl rotation on the dnmr time scale (eq 1).



(1)

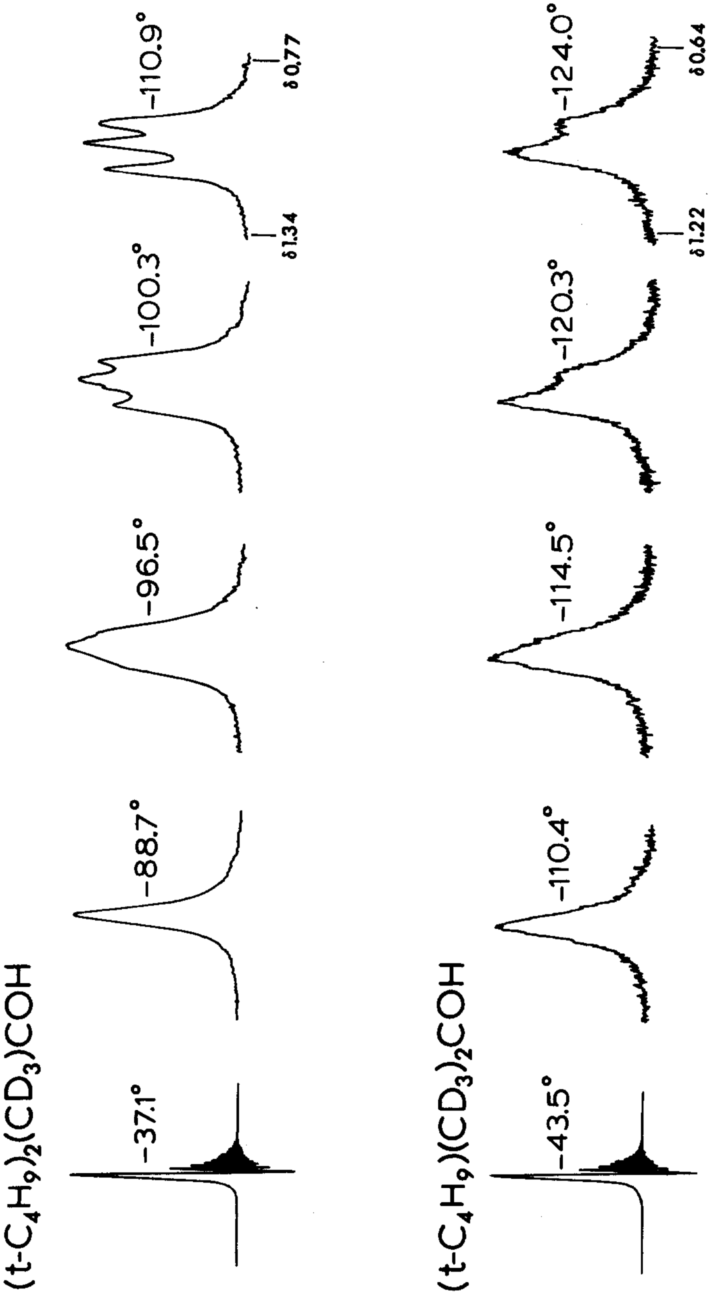

(t-C$_4$H$_9$)$_2$(CD$_3$)COH
-37.1°
-88.7°
-96.5°
-100.3°
-110.9°
δ1.34
δ0.77
(t-C$_4$H$_9$)(CD$_3$)$_2$COH
-43.5°
-110.4°
-114.5°
-120.3°
-124.0°
δ1.22
δ0.64

Table. ^{1}H DNMR Chemical Shifts at Slow Exchange and Free Energies of Activation for tert-Butyl Rotation in Deuteriated Acyclic Alcohols and Other Selected Compounds

compound	^{1}H dnmr chemical shifts for t-C_4H_9 at slow exchange, ppm	solvent	ΔG‡,kcal/mol (temp. °C)
$(t\text{-}C_4H_9)(CD_3)_2COH$	0.873(3H);0.969(6H)	4% by wt. in CH_2CHCl	8.4±0.1(-114.5°)
$(t\text{-}C_4H_9)(CD_3)(C_2D_5)COH$	0.843(3H);0.940(3H); 0.987(3H)	4% by wt. in CH_2CHCl	8.9±0.1(-109.9°)
$(t\text{-}C_4H_9)(CD_3)(C_6H_5CH_2)COH$	0.961(6H);1.045(3H)	4% by wt. in CH_2CHCl	8.9±0.1(-111.9°)
$(t\text{-}C_4H_9)_2(CD_3)COH$	0.980(3H);1.046(3H); 1.129(3H)	4% by wt. in CH_2CHCl	9.6±0.1(-94.6°)
	0.946(3H);1.021(3H); 1.112(3H)	4% by wt. in 60% $(CH_3)_2O$/ 40% $(CH_3)_2NCHO$	9.5±0.1(-94.7°)
	0.955(3H);1.043(3H); 1.120(3H)	4% by wt. in 90% CH_2CHCl/ 10% CD_3OD	9.7±0.1(-90.4°)
$(t\text{-}C_4H_9)(CH_3)_2CH$	0.933(6H);0.750(3H)	5%(v/v) in $CBrF_3$	6.9(-134°; See ref. 2d)
$(t\text{-}C_4H_9)(CH_3)_2CF$	———	———	8.0(See ref.2c)
$(t\text{-}C_4H_9)(CH_3)_2CCl$	———	———	10.4(See ref.2bc)
$(t\text{-}C_4H_9)(CH_3)_2CBr$	———	———	10.7(See ref.2bc)
$(t\text{-}C_4H_9)(CH_3)_2CI$	———	———	11.1(See ref.2c)

Upon lowering the temperature, the tert-butyl peak of $(t\text{-}C_4H_9)_2(CD_3)COH$ broadened and separated into three resolved singlet resonances consistent with slow tert-butyl rotation on the dnmr time scale and a different environment experienced by each of the three methyls of the tert-butyl group(eq 1). The observation of three singlet resonances for tert-butyl is also consistent with fast rotation of the individual methyls of tert-butyl.[3] The slow exchange tert-butyl ^{1}H dnmr chemical shifts and the free energy of activation (ΔG‡) for tert-butyl rotation at or near the dnmr coalescence temperature (as determined from a complete dnmr line shape analysis) are compiled in the Table. In a similar manner, the tert-butyl ^1H dnmr spectrum of $(t\text{-}C_4H_9)(CD_3)_2COH$ separated at low temperatures into two singlet resonances at $\delta 0.873(3H)$ and $\delta 0.969(6H)$ consistent with the symmetry experienced by a static tert-butyl(Figure). Dnmr parameters and free energies of activation for tert-butyl rotation in other alcohols are compiled in the Table.

A perusal of the barriers to tert-butyl rotation in the alcohols compiled in the Table reveals a clear dependence on the steric bulk sequence: $CD_3 < C_2D_5 \sim C_6H_5CH_2 < t\text{-}C_4H_9$ established in other systems.[4] A comparison of the rate of tert-butyl rotation in $(t\text{-}C_4H_9)(CD_3)_2COH$ to the hydrogen and halogen analogues (Table) reveals —OH to be slightly more hindering than—H, about the same as —F, and progressively less hindering than —Cl, —Br, and —I. The Table also indicates the rate of tert-butyl rotation in $(t\text{-}C_4H_9)_2(CD_3)COH$ to be relatively insensitive to three different solvent systems employed.

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