Direct Observation of Hindered t-Butyl Rotation in Neopentyl Bromide and Neopentyl Iodide

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Summary The variable temperature ^{1}H n.m.r. spectra of neopentyl bromide and iodide from -150 to -170 °C show changes in the respective t-butyl resonances consistent with slowing t-butyl rotation on the n.m.r. time scale.

SIMPLE neopentyl derivatives have been important in investigations of organic reaction mechanisms such as S_N2 processes. Although there have been a number of reports concerning restricted rotation about carbon–carbon single bonds in relatively hindered halogenated methylbutanes,[1] there have been no papers concerning the rate of t-butyl rotation in the simple neopentyl halides.

The ^{1}H n.m.r. spectrum (60 MHz) at -91 °C of neopentyl iodide (I) (3% solution, v/v, in $CBrF_3$) showed singlet resonances for the methylene (δ 3·15) and t-butyl (1·12) groups. Below -150 °C, the t-butyl resonance broadens and separates at *ca.* -166 °C into two singlets at δ 1·27 (3H) and 1·05 (6H) consistent with slowing t-butyl rotation on the n.m.r. time scale and the symmetrical environment of a static t-butyl group. The observation of a singlet resonance for each t-butyl Me group of (I) at -166 °C may be rationalized in terms of rapid rotation of individual methyl groups[2] even at that temperature. The methylene resonance of (I) remains a singlet albeit broadened by increasing viscosity at very low temperatures consistent with the three-fold symmetry of the adjacent t-butyl group. Neopentyl bromide (5% solution in $CBrF_3$) behaved similarly although the chemical shift difference between the t-butyl methyl resonances at δ 1·17 (3H) and 1·07 (6H) under conditions of slow exchange (-168 °C) is smaller compared to (I). The t-butyl ^{1}H resonance of neopentyl chloride (3% solution in $CBrF_3$) showed no separation even at -178 °C. Since bromine is somewhat more effective than chlorine in restricting rotation,[1] the absence of separation for neopentyl chloride could be due to a lower barrier than for the bromine and iodine analogues or to a smaller chemical shift difference between different t-butyl methyl groups.

TABLE

Activation parameters for t-butyl rotation

	Bu^tCH_2Br	Bu^tCH_2I
$\Delta H^\ddagger$ (kJ mol^{-1})	$25·1 \pm 0·8$	$24·7 \pm 0·8$
$\Delta S^\ddagger$ (J K^{-1} mol^{-1})	0 ± 2	0 ± 2

Activation parameters for t-butyl rotation in neopentyl iodide and bromide were determined by complete n.m.r. line shape analyses at various temperatures using a locally modified version of the DNMR3[3] program (see Table). The barriers to t-butyl rotation in the two neopentyl halides are, as expected, lower than those in Bu^tCMe_2Cl ($\Delta G^\ddagger$ 41·0 kJ mol^{-1} at -81 °C)[1] and Bu^tCMe_2Br ($\Delta G^\ddagger$ 45·2 kJ mol^{-1} at -68 °C).[1b] The similarity in the barriers to t-butyl rotation in neopentyl bromide and iodide is reminiscent of the preferences for the equatorial conformation in bromocyclohexane ($\Delta G°$ $-2·00$ kJ mol^{-1} at -80 °C) and iodocyclohexane ($\Delta G°$ $-1·97$ kJ mol^{-1} at -80 °C).[4]

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