

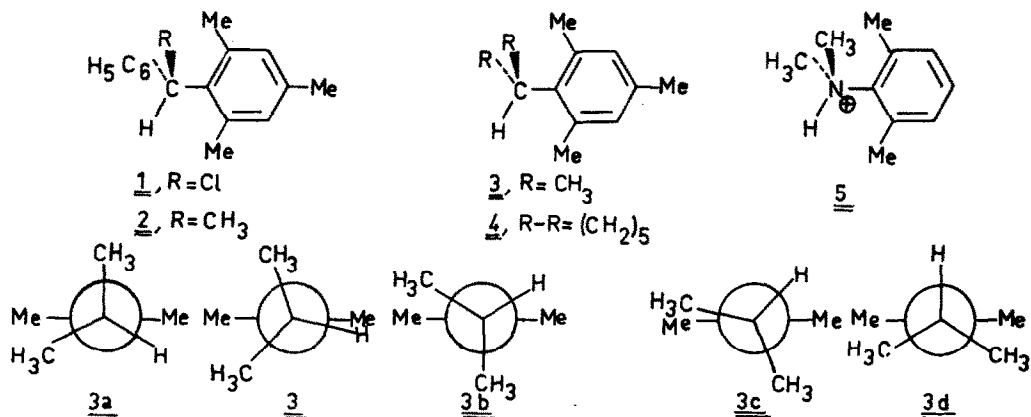
THE CONFORMATION OF 1.3.5-TRIMETHYL-2-ISOPROPYL-BENZENE
AND OF SIMILAR COMPOUNDS CONTAINING sp^2-sp^3 BONDS

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Hassner and Nash ¹⁾ have mentioned that the ¹H-NMR spectrum of 1.3.5-trimethyl-2-(*o*-chlorobenzyl)-benzene (1) at low temperature shows restricted rotation of the mesityl group. We have measured the free enthalpy of activation for this process by coalescence of the 1- and 5-methyl signals ($\tau = 7.53$ and 8.13, -55°, d_6 -acetone) and found $\Delta G_C^\ddagger = 11.3 \pm 0.3$ kcal mole⁻¹ (-45°, d_6 -acetone) and 11.4 ± 0.3 kcal mole⁻¹ (-43.5°, CS₂) ²⁾. This spectral change does not seem to be due to the breaking of the C-Cl bond, as we obtained nearly the same barrier for 2 (11.2 ± 0.3 kcal mole⁻¹, -44.5°, CS₂). Very recently, we learned about results for similar derivatives of fluorene ³⁾ and for benzhydryl-mesitylene ⁴⁾.



As to the conformations involved, more experimental evidence is available for the title compound 2. In d_6 -acetone it shows 1- and 5-methyl singlets at $\tau = 7.68$ and 7.77 (-60°) and $\Delta G_C^\ddagger = 12.8 \pm 0.2$ kcal mole⁻¹ (-35°). The methyl doublet ($J = 7$ cps) of the isopropyl group is not broadened at -60° in d_6 -acetone ($\tau = 8.75$) or in CS₂ ($\tau = 8.77$) as solvents. These findings are com-

patible only with $\underline{3}$ or with rapidly interconverting species $\underline{3a}$ and $\underline{3b}$ as ground state conformations. The downfield shift of the methine septet ($\tau = 6.71$, $+36^\circ$, CS_2), compared with that of isopropyl-benzene ($\tau = 7.05$), leads us to prefer conformation $\underline{3}$ to the $\underline{3a}/\underline{3b}$ equilibrium. The transition state of this C-aryl rotation is probably $\underline{3c}$, not $\underline{3d}$. — The barrier is increased to 14.4 ± 0.3 kcal mole $^{-1}$ (-1.5° , d_6 -acetone) in 1.3.5-trimethyl-2-cyclohexylbenzene ($\underline{4}$).

Anilinium ion $\underline{5}$ was studied by recording the spectra of the corresponding aniline in CF_3COOH (0.3 mole l^{-1}) and proved to be stereochemically similar to its carbon analogue $\underline{3}$. Thus, at -5° the N-methyl doublet ($\tau = 6.39$, $J = 5.5$ cps) and the C-methyl singlets ($\tau = 7.27$ and 7.40) were not broadened. At $+70^\circ$ the latter had coalesced to one sharp signal ($\tau = 7.36$), whereas the N-methyl doublet was completely unaltered. We conclude that the exchange of the N-H proton in $\underline{5}$ is slow⁵⁾ at this temperature and that the coalescence of the C-methyl singlets is due to N-aryl rotation⁶⁾. The ΔG_C^\ddagger -value is considerably higher for $\underline{5}$ (15.9 ± 0.3 kcal mole $^{-1}$, $+26^\circ$, CF_3COOH) than for hydrocarbon $\underline{3}$ (12.8 kcal mole $^{-1}$), thus reflecting the shorter N-aryl bond in anilinium ions compared with the longer C-aryl bond in toluenes.

Work is in progress to alter the substituents in $\underline{3}$, especially with regard to the equilibrium constants between rotamers⁶⁾. — We gratefully acknowledge experimental assistance by Miss J.Linß and Mrs.G.Rissmann.

1) A.Hassner and E.G.Nash, Tetrahedron Letters 1965, 525.

2) At 60 Mcps. ΔG_C^\ddagger -values were calculated assuming a twofold barrier.

3) E.A.Chandross and C.F.Sheley, Jr., J.Am.Chem.Soc. 90, 4345 (1968); T.H. Siddall, III and W.E.Stewart, Tetrahedron Letters 1968, 5011 and personal communication.

4) H.Kessler, A.Mcosmayer and A.Rieker, personal communication.

5) Slow exchange of the NH proton of $\underline{5}$ in CF_3COOH is in accord with the investigation of similar ions by W.F.Reynolds and T.Schaefer, Can.J.Chem. 42, 2641 (1964), if the low acidity of $\underline{5}$ is taken into account: H.C.Brown and A.Cahn, J.Am.Chem.Soc. 72, 2939 (1950).

6) Cf. A.Mannschreck and H.Münsch, Tetrahedron Letters 1968, 3227.