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## Bicyclo[1.1.1]pent-1-yl: A Tertiary Alkyl Radical with Enhanced Reactivity<sup>1</sup>

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Abstract: Absolute rate constants for reactions of bicyclo[1.1.]pent-1-yl radicals with  $\alpha$ -methylstyrene (1.4 x 10<sup>7</sup> M<sup>-1</sup> s<sup>-1</sup>) and 1,4-cyclohexadiene (4.6 x 10<sup>5</sup> M<sup>-1</sup> s<sup>-1</sup>) at 25° C were measured by laser flash photolysis. This bridgehead radical is more reactive than *tert*-butyl which we attribute to its high *s*-character and the absence of steric shielding of the radical center. Copyright © 1996 Elsevier Science Ltd

Bridgehead radicals with cages composed of small rings are necessarily pyramidal. They are expected to be more reactive generally than acyclic *tert*-alkyl radicals, such as the essentially planar *tert*-butyl,<sup>3</sup> because pyramidalization reduces steric shielding of the radical center and reduces radical stabilization via  $HC_{\beta}C_{\alpha}^{\bullet}$  hyperconjugation. Pyramidalisation also increases the *s*-character of the SOMO, as is reflected by enhanced  ${}^{13}C_{\alpha}$  hyperfine splittings ( $a^{13}C$ ), and increases nucleophilicity<sup>4</sup>. Surprisingly, no attempt would appear to have been made to provide quantitative kinetic data which would reveal the magnitude of the enhanced reactivity of small ring bridgehead radicals<sup>5</sup>.

The bicyclo[1.1.1]pent-1-yl radical, 1, is the most extreme example of "bridgehead character" known to date<sup>8</sup>. Recent work has shown that this radical (generated in chain reactions involving [1.1.1]propellane) is active in atom abstraction<sup>9</sup> and addition reactions<sup>10,11</sup> and has high structural integrity<sup>12</sup>. Radical 1 has  $a^{13C} = 223 \text{ G}^{13}$  which is not much lower than the 272 G of the tetrahedral CF<sub>3</sub><sup>•</sup> radical<sup>14</sup> and is dramatically larger than  $a^{13C}$  for *tert*-butyl (45G)<sup>3</sup>. The C<sub>β</sub>C<sub>α</sub><sup>•</sup>C<sub>β</sub> angle in 1 is close to 90<sup>o</sup> <sup>15</sup> (vs. 109<sup>o</sup> for a tetrahedral radical and 120 for a planar radical). Herein we report preliminary kinetic data for two prototypical reactions of 1 and compare these results with literature data for the same reactions of *tert*-butyl.



Radical 1 was generated "instantaneously" by 308 nm laser flash photolysis of the diacyl peroxide  $2^{16}$  (67 mM in CFCl<sub>2</sub>CF<sub>2</sub>Cl). Its addition to  $\alpha$ -methylstyrene ( $\alpha$ -MS) at 25°C was monitored by the pseudo-first-order growth  $k_{expl1}$  of the absorption at 320 nm due to the benzylic radical adduct, 3. A plot of  $k_{expl1}$  vs. [ $\alpha$ -MS] (range 0.04 - 0.17 M) was linear (<r> = 0.9994) and yielded  $k^1(\alpha$ -MS) = 1.4 x 10<sup>7</sup> M<sup>-1</sup> s<sup>-1</sup>. This rate constant is 200 times greater than that reported for addition of the *tert*-butyl to  $\alpha$ -MS, viz., <sup>18</sup>  $k^{Me}3^{C}(\alpha$ -MS) = 7 x 10<sup>4</sup> M<sup>-1</sup> s<sup>-1</sup> at 25 °C.

The rate constant for H-atom abstraction from cyclohexa-1,4-diene (CHD) was determined directly by monitoring the growth of the cyclohexadienyl radical, 4, at 317 nm,  $k^{1}$ (CHD) = 4.5 x 10<sup>5</sup> M<sup>-1</sup> s<sup>-1</sup>, and indirectly using Scaiano *et al's*<sup>19</sup> "probe" technique (with  $\alpha$ -MS as the probe),  $k^{1}$ (CHD) = 4.7 x 10<sup>5</sup> M<sup>-1</sup> s<sup>-1</sup>. This rate

constant is 50-fold larger than that reported for the corresponding H-atom abstraction by *tert*-butyl, viz.<sup>20</sup>  $k^{\text{Me}_3\text{C}}(\text{CHD}) = 9.4 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  at 27°C.

Our absolute kinetic data demonstrate that 1 is, indeed, considerably more reactive than *tert*-butyl. However, these data were severely limited in scope by the difficult synthesis of 2. We trust that the present results will be expanded to produce a much more complete picture of 1's reactivity using standard competitive kinetic methods combined with chain reactions of the much more readily prepared [1.1.1]propellane<sup>10</sup>.

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