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Bicyclo[1.1.1]pent-1-yl: A Tertiary Alkyl Radical with Enhanced Reactivity[1]

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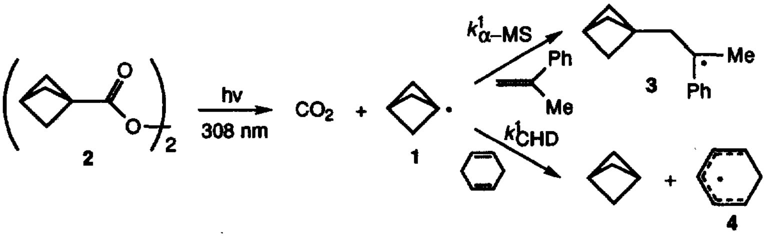
Abstract: Absolute rate constants for reactions of bicyclo[1.1.1]pent-1-yl radicals with α-methylstyrene (1.4 x 10^7 M^{-1} s^{-1}) and 1,4-cyclohexadiene (4.6 x 10^5 M^{-1} s^{-1}) at 25° C were measured by laser flash photolysis. This bridgehead radical is more reactive than *tert*-butyl which we attribute 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,[3] 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^{13C}), and increases nucleophilicity[4]. 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[5].

The bicyclo[1.1.1]pent-1-yl radical, **1**, is the most extreme example of "bridgehead character" known to date[8]. Recent work has shown that this radical (generated in chain reactions involving [1.1.1]propellane) is active in atom abstraction[9] and addition reactions[10,11] and has high structural integrity[12]. Radical **1** has a^{13C} = 223 G[13] which is not much lower than the 272 G of the tetrahedral $CF_3^\bullet$ radical[14] and is dramatically larger than a^{13C} for *tert*-butyl (45G)[3]. The $C_\beta C_\alpha^\bullet C_\beta$ angle in **1** is close to 90° [15] (vs. 109° 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 $CFCl_2CF_2Cl$). Its addition to α-methylstyrene (α-MS) at 25°C was monitored by the pseudo-first-order growth k_{exptl} of the absorption at 320 nm due to the benzylic radical adduct, **3**. A plot of k_{exptl} vs. [α-MS] (range 0.04 - 0.17 M) was linear (<r> = 0.9994) and yielded k^1(α-MS) = 1.4 x 10^7 M^{-1} s^{-1}. This rate constant is 200 times greater than that reported for addition of the *tert*-butyl to α-MS, viz.,[18] k^{Me_3C}(α-MS) = 7 x 10^4 M^{-1} s^{-1} 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 10^5 M^{-1} s^{-1}, and indirectly using Scaiano *et al's*[19] "probe" technique (with α-MS as the probe), k^1(CHD) = 4.7 x 10^5 M^{-1} s^{-1}. This rate constant is 50-fold larger than that reported for the corresponding H-atom abstraction by *tert*-butyl, viz.[20] $k^{\mathrm{Me_3C}}(\mathrm{CHD}) = 9.4 \times 10^3\ \mathrm{M^{-1}\ s^{-1}}$ 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[10].

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