

CARBON-13 NUCLEAR MAGNETIC RESONANCE OF STRAINED OLEFINS

W. M. Beckenbaugh, S. R. Wilson and P. A. Loeffler\*

Rice University, Houston, Texas 77001

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While carbon-13 nuclear magnetic resonance (CMR) studies of complex organic molecules<sup>1</sup> are now becoming routine, too little interest has been focused on the use of cmr for investigating strained olefins.<sup>2</sup> Prompted by a recent report by Mock<sup>3</sup> we present data which relates strain to the <sup>13</sup>C chemical shift of the olefinic carbons.

Mock has proposed a modest rehybridization of the 2p<sub>π</sub> molecular orbitals incorporating increased s character in the bond. Since cmr has been conclusively shown to be a sensitive probe of hybridization, factors relating torsionally induced rehybridization and chemical shift provide a direct experimental test of Mock's hypothesis. In reference to cis- and trans-di-t-butylethylene sizable variation in the chemical shift of the olefinic carbons demonstrates a change in hybridization due to torsional strain in the cis structure. Note from the table the chemical shift difference ( $\delta_{\text{cis}} - \delta_{\text{trans}}$ ) in di-t-butylethylene is 8.2 ppm. One can compare this to the chemical shift difference in cis and trans-2-butene of 1.4 ppm. This is qualitatively proportional to the difference in strain between the two pairs of isomers.<sup>5</sup> Though we are not implying that all the strain energy is localized in the π bond.<sup>2,5</sup>

However the difference in chemical shift between cis- and trans-cyclooctene is but 4.2 ppm. Since cis-di-t-butylethylene and trans-cyclooctene have the same estimated strain energy, ~9 kcal/mole,<sup>4,5</sup> the chemical shift difference of 8.2 and 4.2 ppm may evidence support for Mock's hypothesis that trans-cyclooctene has expanded lobes on the same face of the double bond and

consequently greater accessibility than in cis-di-t-butylethylene which has expanded lobes on opposite faces.<sup>7</sup> In addition, one notes that the olefinic chemical shift of the more strained compound of a cis-trans pair is usually upfield. In the case of cis and trans-cyclooctene this trend is not observed. Thus the different types of rehybridization for cis-di-t-butylethylene and trans-cyclooctene are reflected in CMR.

Further study of strained olefins is required for a more quantitative evaluation of the effects of strain on carbon-13 chemical shift. Investigations of sterically hindered olefins, dienes and trienes is now in progress in this laboratory.

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Table I  
Carbon Chemical Shift ( $\delta_{CS_2}$ )

Compound	1	2	3	4	$\Delta H$ (Hydrogenation) kcal/mole <sup>5</sup>
<u>trans</u> -2-butene	67.7 <sup>6</sup>	176.1			27.6
<u>cis</u> -2-butene	69.1 <sup>6</sup>	181.6			28.6
<u>trans</u> -di- <u>t</u> -butylethylene	57.5	160.9	163.4		26.8
<u>cis</u> -di- <u>t</u> -butylethylene	65.7	164.1	172.4		36.2
<u>trans</u> -cyclooctene	59.7 <sup>6</sup>	158.2	158.2	163.8	32.2
<u>cis</u> -cyclooctene	63.9	163.9	166.9	167.7	23.0

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