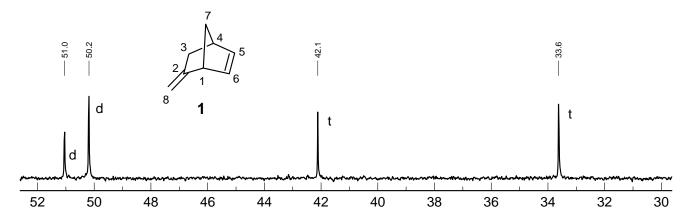
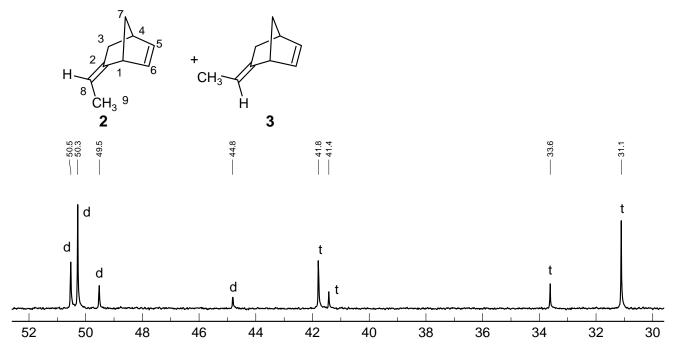


**Problem R-03E**. Below are given the aliphatic carbons of <sup>13</sup>C NMR spectra of 2-methylenebicyclo[2.2.1]heptene, and the <sup>13</sup>C NMR spectrum of a mixture of stereoisomeric 2-ethylidenebicyclo[2.2.1]heptenes (complete spectra are shown on the following page). Your task is to assign some of the resonances and determine which isomer is which in the mixture of isomers. (Source: Aldrich Spectra Viewer).

(a) Assign the aliphatic signals of 1 by writing the  $\delta$  values next to the appropriate carbons



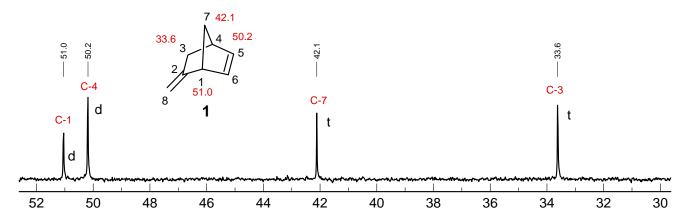
(b) Assign the aliphatic signals of compounds  ${\bf 2}$  and  ${\bf 3}$  by writing the  $\delta$  values next to the appropriate carbons



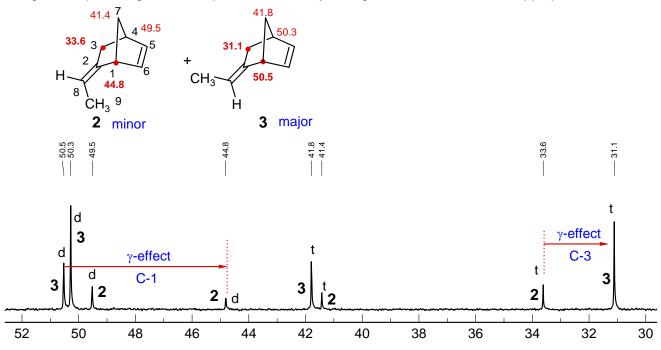
(c) Which isomer (2 or 3) is the major one?\_\_\_\_\_ Briefly explain the basis for your assignment of structure. Be specific. Use the numbering scheme shown in your answer.

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(a) Assign the aliphatic signals of 1 by writing the  $\delta$  values next to the appropriate carbons



(b) Assign the aliphatic signals of compounds 2 and 3 by writing the  $\delta$  values next to the appropriate carbons



(c) Which isomer (2 or 3) is the major one? \_\_\_\_3 Briefly explain the basis for your assignment of structure. Be specific. Use the numbering scheme shown in your answer.

In compound 3, C-3 should see a  $\gamma$ -effect and be upfield of C-3 in 1 and 2. The minor isomer has a C-3 chemical shift almost identical to that of 1, thus it must be 2. The major isomer is then 3. Similar argument for C-1, which should be upfield in 2 compared to those in 1 and 3. Chemical shifts for C4 and C-7 should be close in both isomers.