
(a) The 60 MHz \(^1\text{H} \text{NMR}\) spectrum of phosphoenolpyruvate (PEP) is shown below. Analyze the multiplets and assign the couplings.

(b) The 100 MHz \(^1\text{H} \text{NMR}\) spectrum of PEP labeled 60% with \(^{13}\text{C}\) at the carboxyl carbon is shown below. Analyze the multiplets and assign the chemical shifts and couplings.

(c) The 60 MHz \(^1\text{H} \text{NMR}\) spectrum of PEP labeled with one deuterium atom is shown below. Draw the structure of the compound, include stereochemistry.

(a) The 60 MHz \(^1H\) NMR spectrum of phosphoenolpyruvate (PEP) is shown below. Analyze the multiplets and assign the couplings

\[
\text{\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{spectrum_a.png}
\caption{60 MHz \(^1H\) NMR spectrum of phosphoenolpyruvate.}
\end{figure}}
\]

**HA and HB are coupled to each other \((^2J_{HH})\), and each is coupled to the \(^{31}P\) \((^4J_{HP})\) by equal coupling constants \((1.5 \text{ Hz})\), giving apparent triplets for each proton. Note that the related \(^4J_{H-H}\) allylic coupling \((HC=C-CH\) compared with \(^4J_{H-P}\) \(HC=C-OP\)) is also largely independent of double bond stereochemistry.**

(b) The 100 MHz \(^1H\) NMR spectrum of PEP labeled 60% with \(^{13}C\) at the carboxyl carbon is shown below. Analyze the multiplets and assign the chemical shifts and couplings.

\[
\text{\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{spectrum_b.png}
\caption{100 MHz \(^1H\) NMR spectrum of phosphoenolpyruvate labeled with \(^{13}C\).}
\end{figure}}
\]

\[^3J_{HC(cis)} = 3 \text{ Hz} \quad \text{HA}\]
\[^3J_{HC(trans)} = 9.5 \text{ Hz} \quad \text{HB}\]

**The central peaks are from the 40% of the sample that has \(^{12}C\) at the carboxyl carbon, the satellites are from the 60% \(^{13}C\).**

**This allows assignment of the two protons - the upfield one with the large \(^3J_{HC}\) is trans to the carboxyl group (HB) and the other HA (\(^3J_{H-C(trans)}\) is always larger than \(^3J_{H-C(cis)}\)).**

(c) The 60 MHz \(^1H\) NMR spectrum of PEP labeled with one deuterium atom is shown below. Draw the structure of the compound, include stereochemistry.

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\text{\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{spectrum_c.png}
\caption{60 MHz \(^1H\) NMR spectrum of phosphoenolpyruvate labeled with a deuterium atom.}
\end{figure}}
\]

\[^2J_{HD}\] is not detectable, since it will be only about \(1.5/6 = 0.2 \text{ Hz}\).