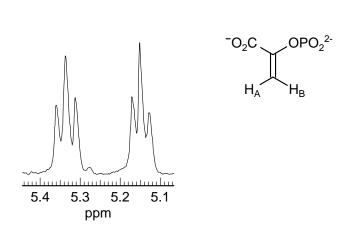
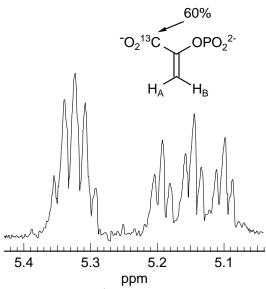
Problem R-85K (C₃H₂O₅P Na₃) Source: J. Am. Chem. Soc. 1970, 92, 4095 (digitized hard copy).

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

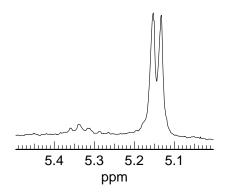


20 10 0 Hz

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

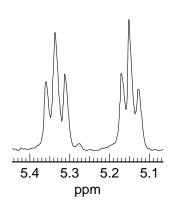


(c) The 60 MHz ¹H NMR spectrum of PEP labeled with one deuterium atom is shown below. Draw the structure of the compound, include stereochemistry.

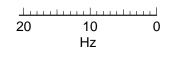


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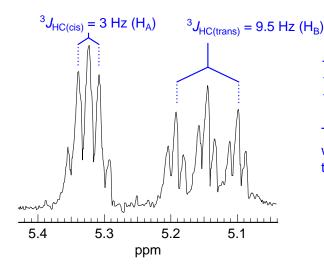


$$O_2$$
 OPO $_3$ OPO $_4$ OPO $_5$ OPO $_5$



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

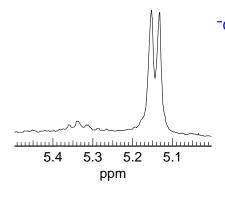
(b) The 100 MHz ¹H NMR spectrum of PEP labeled 60% with ¹³C at the carboxyl carbon is shown below. Analyze the multiplets and assign the chemical shifts and couplings.



The central peaks are from the 40% of the sample that has ¹²C at the carboxyl carbon, the satellites are from the 60% ¹³C.

This allows assignment of the two protons - the upfield one with the large $^3J_{\rm HC}$ is trans to the carboxyl group (H_B) and the other H_A ($^3J_{\rm HC}$ (trans) is always larger than $^3J_{\rm HC}$ (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.



$$O_2C$$
 OPO_3^2 OPO_4

H_A has been mostly replaced by deuterium

 $^2J_{\rm HD}$ is not detectable, since it will be only about 1.5/6 = 0.2 Hz