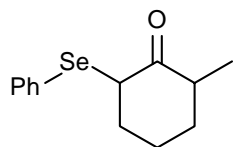


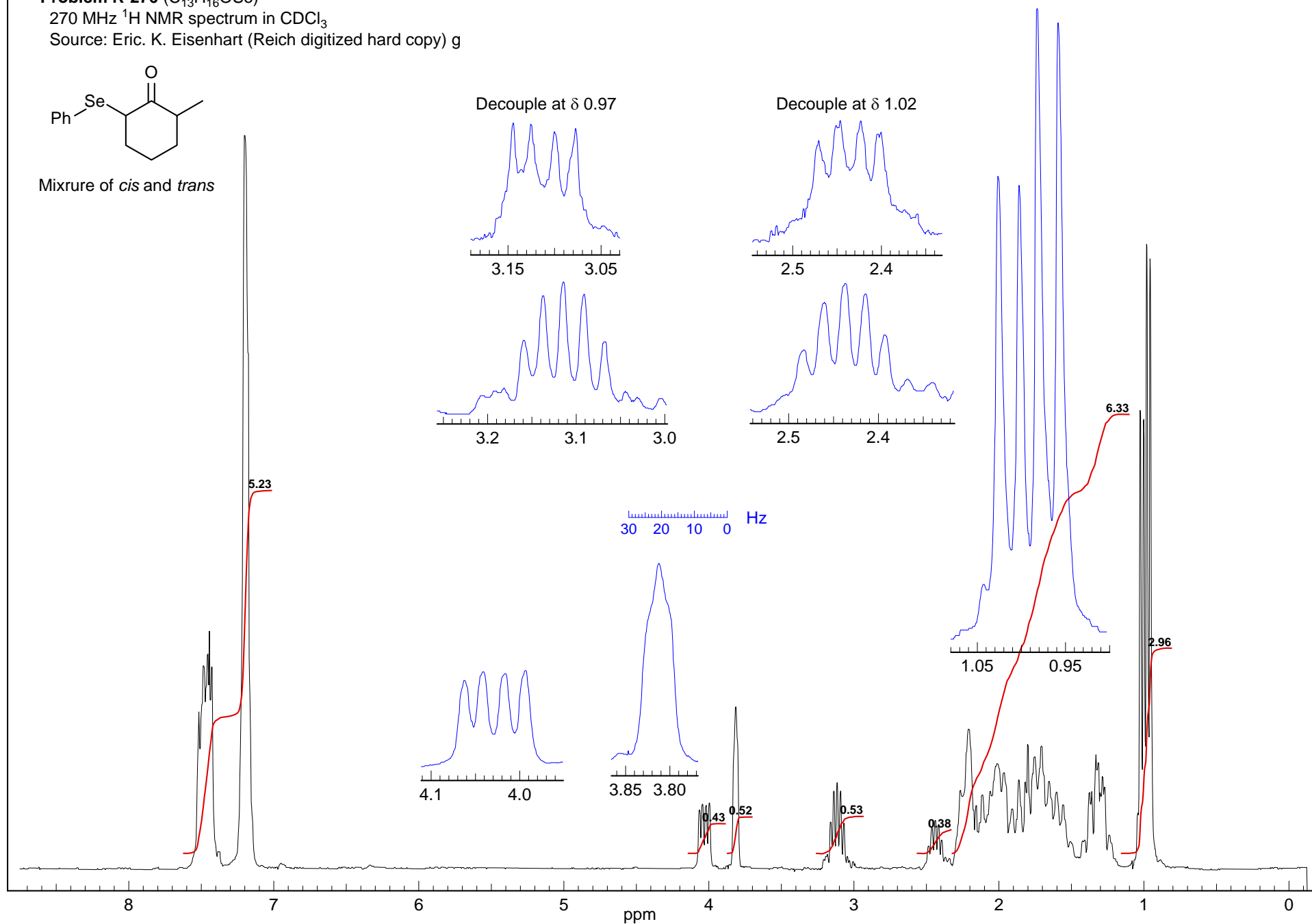
Problem R-276 (C₁₃H₁₆OSe)

270 MHz ¹H NMR spectrum in CDCl₃

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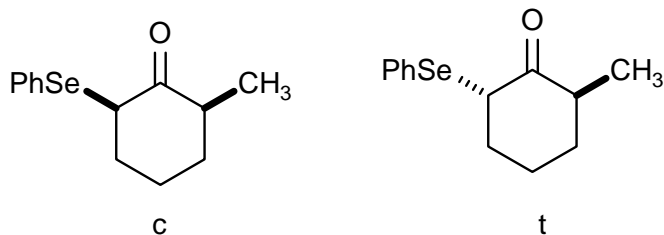


Mixture of *cis* and *trans*



Problem R-276. The ^1H NMR spectrum of a mixture 6-phenylseleno-2-methylcyclohexanones (cis and trans) is shown.

(a) Label each assignable peak in the NMR spectrum as to whether it belongs to the cis (c) or trans (t) isomer. Give your reasoning as to which isomer is which, and give the approximate ratio.



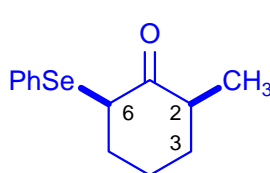
(b) Determine the apparent coupling constants exhibited by the decoupled signals at 3.1 and 2.5 δ . Under what conditions are these true coupling constants (you may assume the decoupling experiment was carried out properly)?

(c) Complete the conformational pictures below for the two isomers of **R-276**. Label as many of the protons as possible with the appropriate δ and J values.

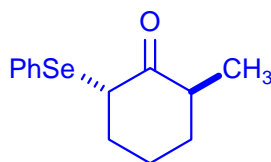


Problem R-276. The ^1H NMR spectrum of a mixture 6-phenylseleno-2-methylcyclohexanones (cis and trans) is shown.

- (a) Label each assignable peak in the NMR spectrum as to whether it belongs to the cis (c) or trans (t) isomer. Give your reasoning as to which isomer is which, and give the approximate ratio.



c
minor
43%



t
Major
57%

The peaks at 2.44 and 3.12 are the C(H)CH_3 signals. They are hard to parse (each should be a dqd), but the spectra with proton decoupling of the CH_3 groups are simpler - both are nearly identical dd, with J of 12 and 6 to the neighboring carbon. Thus the CH_3 group must be largely equatorial in both isomers, with one $J_{\text{ax-eq}}$ (6 Hz) and one $J_{\text{ax-ax}}$ (12 Hz) to the protons at C^3 . The A value of CH_3 is 1.7 kcal/mol, that of PhSe is 1.1 kcal/mol, so this is as expected.

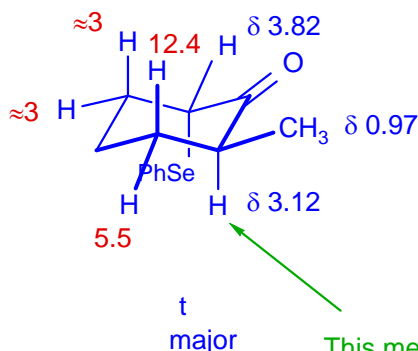
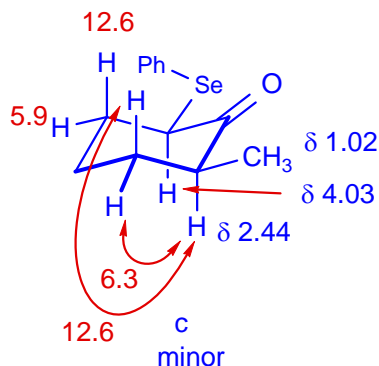
The downfield signals at δ 3.82 and 4.03 are the C(H)SePh protons. The minor isomer at δ 4.03 is a dd, $J = 12, 6$ Hz ($J_{\text{ax-eq}} = 6$ Hz) and one $J_{\text{ax-ax}} = 13$ Hz), therefore an axial proton and an equatorial SePh group. So this is the *cis* isomer. The major isomer is a poorly defined triplet with a small J (≈ 3 Hz), so an equatorial proton with small $J_{\text{eq-eq}}$ $J_{\text{eq-ax}}$ and thus an axial SePh group, the *trans* isomer.

- (b) Determine the apparent coupling constants exhibited by the decoupled signals at 3.1 and 2.5 δ . Under what conditions are these true coupling constants (you may assume the decoupling experiment was carried out properly)?

trans δ 3.12, dd, $J = 12.4, 5.5$ Hz
cis δ 2.44, dd, $J = 12.6, 6.3$

These are true coupling constants only if the gem protons on the neighboring carbons (C^3) are not strongly coupled, i.e. close in chemical shift and thus parts of a "virtually coupled" spin system, where apparent dd give partially (or completely) averaged J values.

- (c) Complete the conformational pictures below for the two isomers of **R-276**. Label as many of the protons as possible with the appropriate δ and J values.



This methyl group is moved unusually downfield by 1,3-diaxial interaction with the PhSe group.

Problem R-276 (C₁₃H₁₆OSe)270 MHz ¹H NMR spectrum in CDCl₃

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