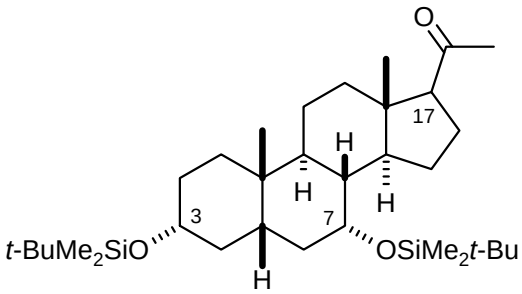
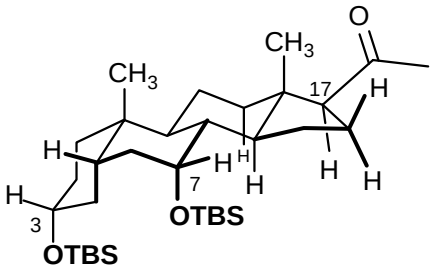
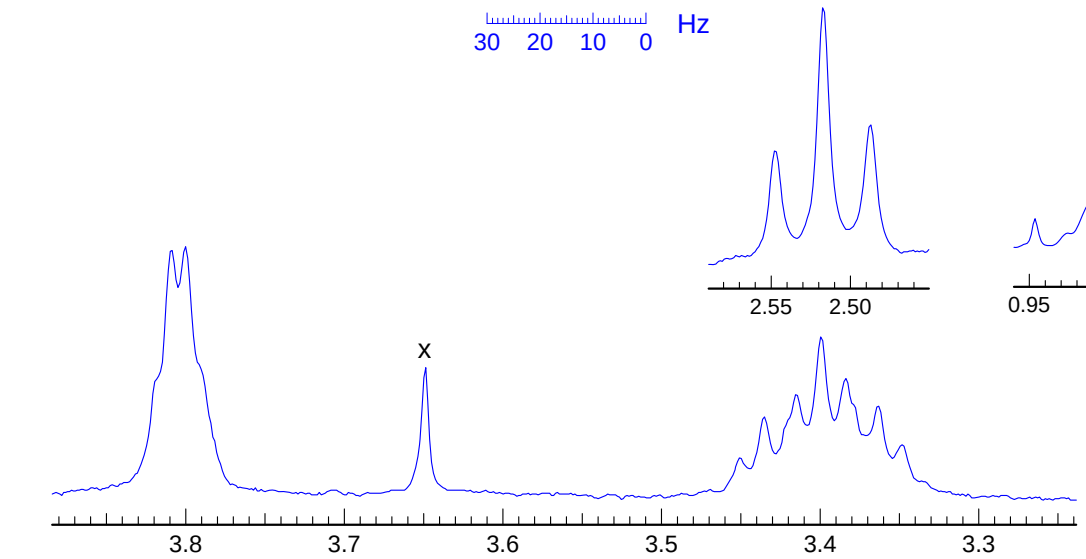
Problem R-09l ($C_{33}H_{62}O_2Si_2$)
300 MHz ^{1}H NMR Spectrum in $CDCl_3$
Source: I. L. Reich, K. Plessel/Reich 040-04 g

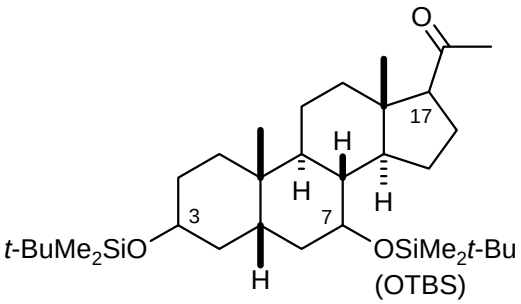


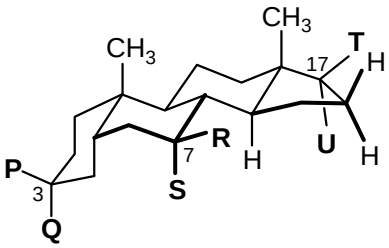




PLT ex-2-2009-10-gq.plt

Problem R-09l This problem requires you to analyze the ^{1}H NMR spectrum of a steroid, and determine the stereochemistry at three centers. A planar projection and conformational drawing is shown below.





(a) Assign the signal at C-3 (δ____). Explain how you identified the signal, and make a stereochemical assignment: P =_____ , Q =_____ (**H** or **OTBS**).

(b) Assign the signal at C-7 (δ____). Explain how you identified the signal, and make a stereochemical assignment: R =_____ , S =_____ (**H** or **OTBS**).

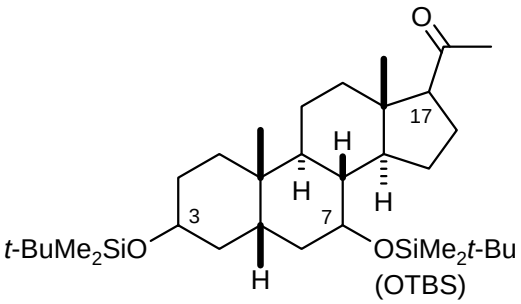
(c) Assign the signal at C-17 (δ____). Explain how you identified the signal, and make a stereochemical assignment: T =_____ , U =_____ (**H** or **$CH_3C(=O)$**).

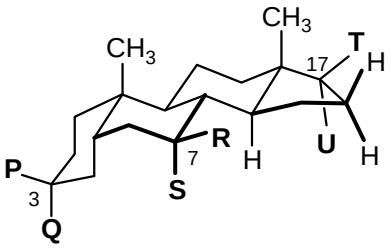
(d) Why is the methyl group at δ 2.1 so much taller (i.e. sharper) than the one at δ 0.6?

(e) Assign and explain the signals at δ 0.00 to 0.10

15

Problem R-09l This problem requires you to analyze the ^{1}H NMR spectrum of a steroid, and determine the stereochemistry at three centers. A planar projection and conformational drawing is shown below.





(a) Assign the signal at C-3 (δ 3.4). Explain how you identified the signal, and make a stereochemical assignment: P = H , Q = OTBS (**H** or **OTBS**).

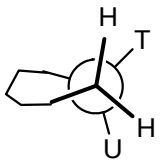
4 The multiplet at δ 3.4 is a tt, J = 11, 4 Hz. This must correspond to two J_{aa} and two J_{ae} couplings, and can only be H-3. H-7 has only 3 neighbors, and H-17 only two. Since there are two large axial couplings, H-3 must be axial, and the OTBS group equatorial.

(b) Assign the signal at C-7 (δ 3.81). Explain how you identified the signal, and make a stereochemical assignment: R = H , S = OTBS (**H** or **OTBS**).

4 This signal is probably a broad quartet, with J = 3 Hz, thus at least 3 nearest neighbors. None of couplings are axial-axial, thus the proton must be equatorial.

(c) Assign the signal at C-17 (δ 2.52). Explain how you identified the signal, and make a stereochemical assignment: T = Ac , U = H (**H** or **$CH_3C(=O)$**).

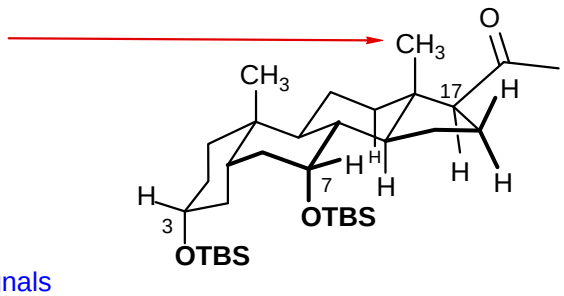
4 This is the only other downfield signal (no other protons are adjacent to a carbonyl group). The signal is a triplet, J = 9 Hz. Examination of the conformation shows that if T = H then one of the couplings should be very small, since Θ is likely to be near 90°. On the other hand, if U = H then both couplings will be fairly large, since one has Θ near 0°, the other with Θ near 180°.



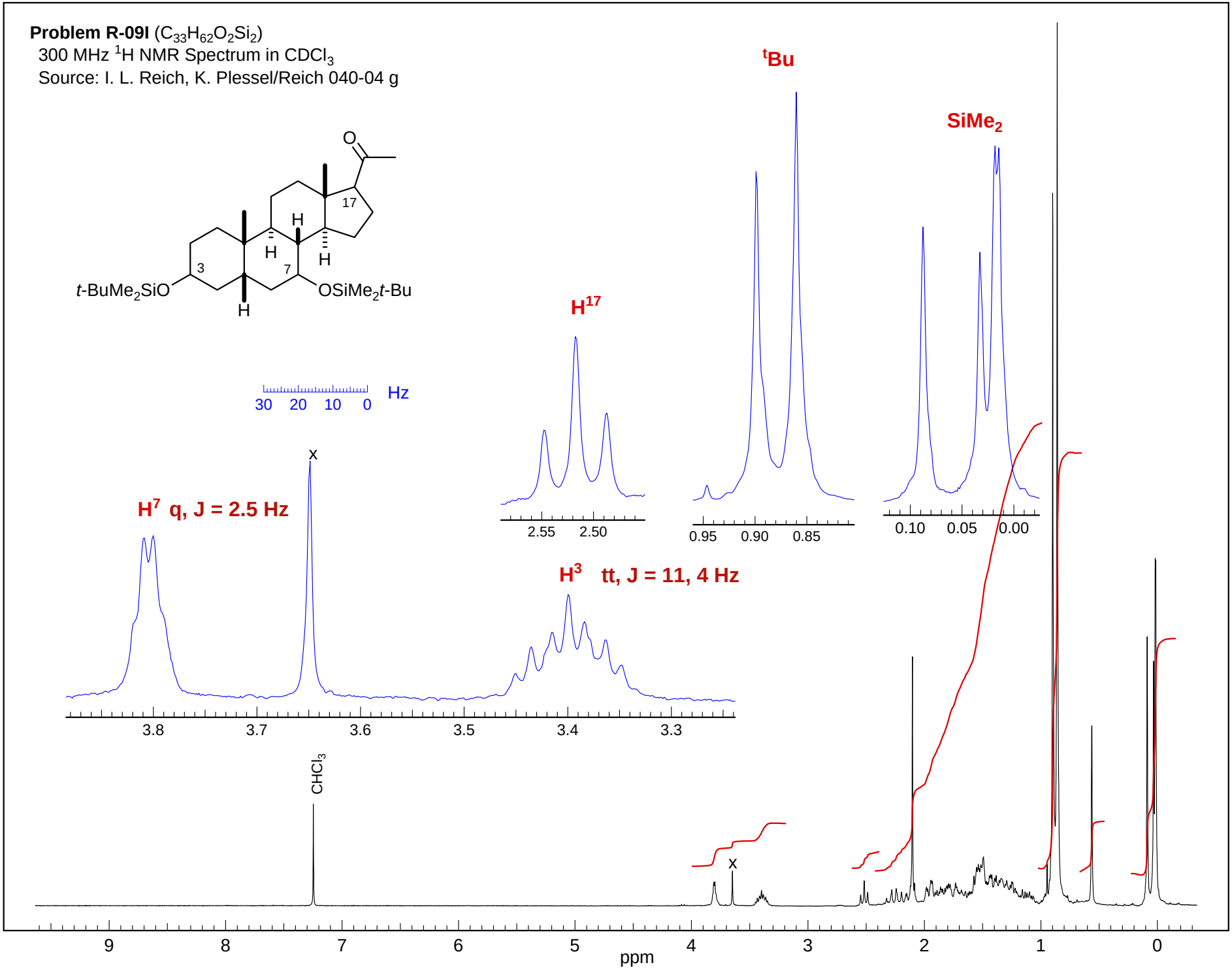
(d) Why is the methyl group at δ 2.1 so much taller (i.e. sharper) than the one at δ 0.6?

1 The ring Me group has small W-couplings to the trans-diaxial protons, the Me-C(=O) group is essentially uncoupled

We don't, however, know which of the bridgehead methyl groups we are looking at, the other one is under the t-butyl signals



(e) Assign and explain the signals at δ 0.00 to 0.10

2 The $SiMe_2$ groups are each diastereotopic, so we see four Me signals

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