Chapter One, Problem A: Generic Chemical Shifts

$C_7H_{14}O$

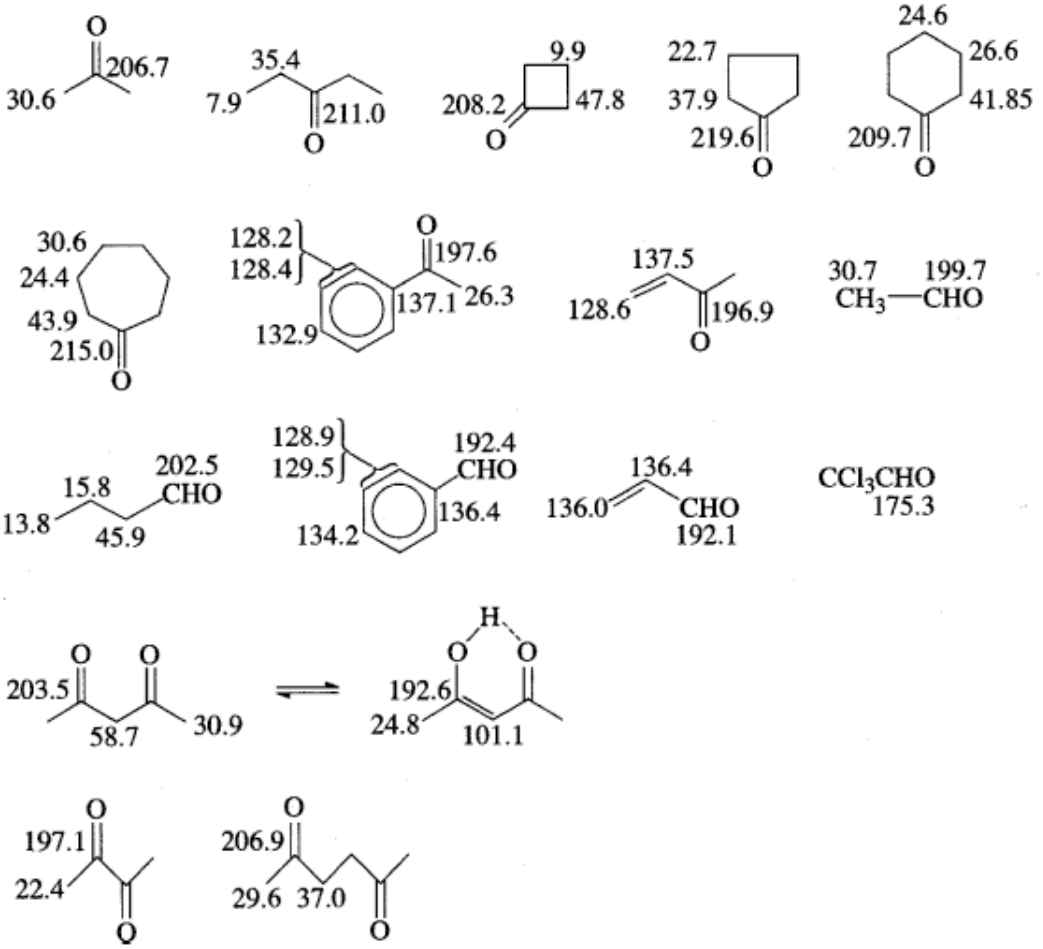
23, q (2)
28, d
29, q
33, t
42, t
206, s

You would like to be able to glance at the ^{13}C data and immediately have diagnostic signals stick out. You will learn to do this by understanding the chemical shift of carbons both within and next to organic functional groups.

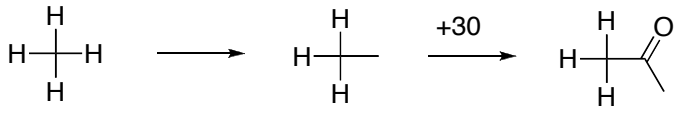
Worksheet, step one: The IHD is calculated by multiplying the number of carbons by two, adding two, then subtracting the number of hydrogens, and dividing by two. In this case, the IHD = 1. All the H's are attached to carbon.

Worksheet, step two: We need to find out the source of the IHD. From the ^{13}C data, there is a signal at 206, which is a singlet, meaning that there are no H's attached to the carbon. From the summary on the worksheet, we know that this is in the carbonyl range. Referring to Table C8, we find that this is a ketone. Note that if it had been an aldehyde, it would have been a doublet, not a singlet.

Table C.8 Shift Positions of the C=O Group and Other Carbon Atoms of Ketones and Aldehydes (ppm from TMS)



Worksheet, Step 2 (Continued) – Exploring around the unsaturated functional groups: Since the unknown is a ketone, there must be a carbon on each side of the carbonyl. To locate these two carbons, we use *generic chemicals shifts*, first approximations of the chemical shift of the carbon. We generate generic chemical shifts by combining the data in Table C10 for the starting hydrocarbon with the data in Table C11 for the α-shift. The carbon next to the ketone has either 0, 1, 2 or 3 H's. If it has 3 H's, it will be a methyl group, and will appear as a quartet in the ^{13}C spectrum. To create a methyl ketone, we start with the hydrocarbon, methane, take off an H, add the ketone, and add the α-shift for ketone carbonyl. The value of –2 comes from Table C10, and the value for the α-shift for ketone comes from Table C11.



methane

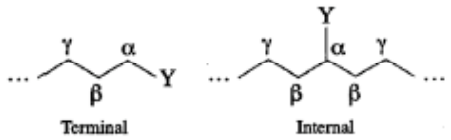
- 2

28, q

Table C.10 The ^{13}C Shifts for Some Linear and Branched-Chain Alkanes (ppm from TMS)

COMPOUND	C-1	C-2	C-3	C-4	C-5
Methane	−2.3				
Ethane	5.7				
Propane	15.8	16.3	15.8		
Butane	13.4	25.2	25.2		
Pentane	13.9	22.8	34.7	22.8	13.9
Hexane	14.1	23.1	32.2	32.2	23.1
Heptane	14.1	23.2	32.6	29.7	32.6
Octane	14.2	23.2	32.6	29.9	29.9
Nonane	14.2	23.3	32.6	30.0	30.3
Decane	14.2	23.2	32.6	31.1	30.5
Isobutane	24.5	25.4			
Isopentane	22.2	31.1	32.0	11.7	
Isohexane	22.7	28.0	42.0	20.9	14.3
Neopentane	31.7	28.1			
2,2-Dimethylbutane	29.1	30.6	36.9	8.9	
3-Methylpentane	11.5	29.5	36.9	(18.8, 3-CH_3)	
2,3-Dimethylbutane	19.5	34.3			
2,2,3-Trimethylbutane	27.4	33.1	38.3	16.1	
2,3-Dimethylpentane	7.0	25.3	36.3	(14.6, 3-CH_3)	

Table C.11 Incremental Substituent Effects (ppm) on Replacement of H by Y in Alkanes



	α		β		γ
Y	TERMINAL	INTERNAL	TERMINAL	INTERNAL	
CH_3	+ 9	+ 9	+ 6	+ 6	−2
$CH=CH_2$	+20		+ 6		−0.5
C CH	+ 4.5		+ 5.5		−3.5
COOH	+21	+16	+3	+ 2	−2
COO^-	+25	+20	+5	+ 3	−2
COOR	+20	+17	+3	+ 2	−2
COCl	+33	28		+ 2	
$CONH_2$	+22		+ 2.5		−0.5
COR	+30	+24	+ 1	+ 1	−2
CHO	+31		0		−2
Phenyl	+23	+17	+ 9	+ 7	−2
OH	+48	+41	+10	+ 8	−5
OR	+58	+51	+ 8	+ 5	−4
OCOR	+51	+45	+ 6	+ 5	−3
NH_2	+29	+24	+11	+10	−5
NH_3	+26	+24	+ 8	+ 6	−5
NHR	+37	+31	+ 8	+ 6	−4
NR_2	+42		+ 6		−3
NR_3	+31		+ 5		−7
NO_2	+63	+57	+ 4	+ 4	
CN	+ 4	+ 1	+ 3	+ 3	−3
SH	+11	+11	+12	+11	−4
SR	+20		+ 7		−3
F	+68	+63	+ 9	+ 6	−4
Cl	+31	+32	+11	+10	−4
Br	+20	+25	+11	+10	−3
I	− 6	+ 4	+11	+12	−1

Applying the same principles, if the C next to the ketone carbonyl has 2 H's, it will be a methylene group, and will appear as a triplet in the ^{13}C spectrum. To create a methylene, we start with the carbon at the end of a chain, take off an H, add the ketone, and add the α-shift for ketone carbonyl. The value of 14 comes from Table C10, and the value for the α-shift for ketone comes from Table C11, above.

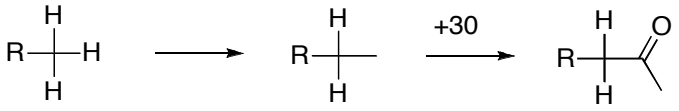
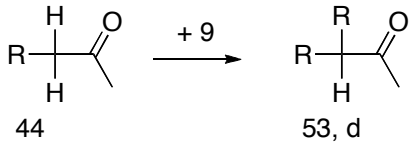


Table C.10 The ^{13}C Shifts for Some Linear and Branched-Chain Alkanes (ppm from TMS)

COMPOUND	C-1	C-2	C-3	C-4	C-5
Methane	−2.3				
Ethane	5.7				
Propane	15.8	16.3	15.8		
Butane	13.4	25.2	25.2		
Pentane	13.9	22.8	34.7	22.8	13.9
Hexane	14.1	23.1	32.2	32.2	23.1
Heptane	14.1	23.2	32.6	29.7	32.6
Octane	14.2	23.2	32.6	29.9	29.9
Nonane	14.2	23.3	32.6	30.0	30.3
Decane	14.2	23.2	32.6	31.1	30.5
Isobutane	24.5	25.4			
Isopentane	22.2	31.1	32.0	11.7	
Isohexane	22.7	28.0	42.0	20.9	14.3
Neopentane	31.7	28.1			
2,2-Dimethylbutane	29.1	30.6	36.9	8.9	
3-Methylpentane	11.5	29.5	36.9	(18.8, 3-CH_3)	
2,3-Dimethylbutane	19.5	34.3			
2,2,3-Trimethylbutane	27.4	33.1	38.3	16.1	
2,3-Dimethylpentane	7.0	25.3	36.3	(14.6, 3-CH_3)	

Once the generic chemical shift for a methylene is calculated, just add +9 to make it into a methine, a doublet in the ^{13}C spectrum, since from Table C11, the α-shift for an alkyl group is + 9. To make a carbon with no H's, a singlet in the ^{13}C spectrum, add another + 9.



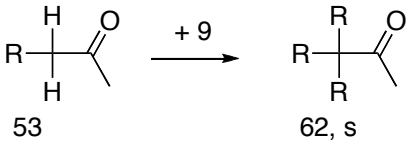
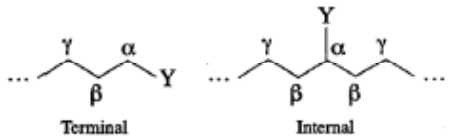


Table C.11 Incremental Substituent Effects (ppm) on Replacement of H by Y in Alkanes

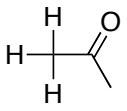


	α		β		γ
Y	TERMINAL	INTERNAL	TERMINAL	INTERNAL	
CH_3	+ 9	+ 9	+ 6	+ 6	−2
$CH=CH_2$	+20		+ 6		−0.5
C CH	+ 4.5		+ 5.5		−3.5
COOH	+21	+16	+3	+ 2	−2
COO^-	+25	+20	+5	+ 3	−2
COOR	+20	+17	+3	+ 2	−2
COCl	+33	28		+ 2	
$CONH_2$	+22		+ 2.5		−0.5
COR	+30	+24	+ 1	+ 1	−2
CHO	+31		0		−2
Phenyl	+23	+17	+ 9	+ 7	−2
OH	+48	+41	+10	+ 8	−5
OR	+58	+51	+ 8	+ 5	−4
OCOR	+51	+45	+ 6	+ 5	−3
NH_2	+29	+24	+11	+10	−5
NH_3	+26	+24	+ 8	+ 6	−5
NHR	+37	+31	+ 8	+ 6	−4
NR_2	+42		+ 6		−3
NR_3	+31		+ 5		−7
NO_2	+63	+57	+ 4	+ 4	
CN	+ 4	+ 1	+ 3	+ 3	−3
SH	+11	+11	+12	+11	−4
SR	+20		+ 7		−3
F	+68	+63	+ 9	+ 6	−4
Cl	+31	+32	+11	+10	−4
Br	+20	+25	+11	+10	−3
I	− 6	+ 4	+11	+12	−1

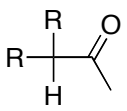
Generic Chemical Shift Tables

The generic chemical shifts are pretty close, usually ± 5. Remember, both chemical shift and multiplicity must match! You will find it useful to make your own tables of generic chemical shifts for the common organic functional groups, for quick ready reference.

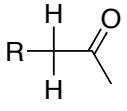
Generic Chemical Shifts: Ketone



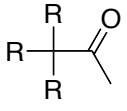
28, q



53, d

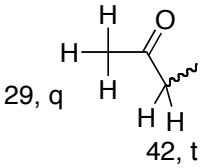


44, t



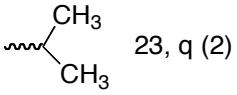
62, s

Returning to Problem A, and applying the generic values we calculated, it is immediately apparent that one side of the ketone is a CH_3, and the other side is a CH_2.

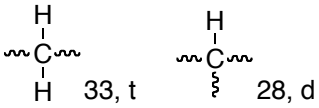


Worksheet, Step 3: There are no more heteroatoms.

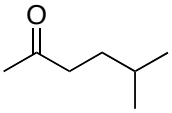
Worksheet, Step 4a: There are two more methyl groups, and they have the same chemical shift, so they are symmetrical. There is no other symmetry in the data, so the two methyl groups must be attached to the same carbon.



Worksheet, Step 4c: There are two more carbons.



Worksheet, Step 5: There is only one way to assemble all the pieces.



More precise chemical shifts: It is possible to use Table C10 and Table C11 to calculate more precise ^{13}C chemical shifts. This is done by using actual hydrocarbons from Table C10, and α, β, and γ shifts from Table C11. To illustrate, using this ketone,

Table C.10 The ^{13}C Shifts for Some Linear and Branched-Chain Alkanes (ppm from TMS)

COMPOUND	C-1	C-2	C-3	C-4	C-5
Methane	−2.3				
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Pentane	13.9	22.8	34.7	22.8	13.9
Hexane	14.1	23.1	32.2	32.2	23.1
Heptane	14.1	23.2	32.6	29.7	32.6
Octane	14.2	23.2	32.6	29.9	29.9
Nonane	14.2	23.3	32.6	30.0	30.3
Decane	14.2	23.2	32.6	31.1	30.5
Isobutane	24.5	25.4			
Isopentane	22.2	31.1	32.0	11.7	
Isohexane	22.7	28.0	42.0	20.9	14.3
Neopentane	31.7	28.1			
2,2-Dimethylbutane	29.1	30.6	36.9	8.9	
3-Methylpentane	11.5	29.5	36.9	(18.8, 3-CH_3)	
2,3-Dimethylbutane	19.5	34.3			
2,2,3-Trimethylbutane	27.4	33.1	38.3	16.1	
2,3-Dimethylpentane	7.0	25.3	36.3	(14.6, 3-CH_3)	

the staring hydrocarbon would be 2-methylpentane, named “isopentane” in the Table.

In Table C11, we are given both “terminal” and “internal” shifts. As in this case we are replacing an H on a methyl group with the ketone, we will use “terminal” shifts from the Table. If we had replaced an H from a methylene or a methine, we would use “internal” shifts.

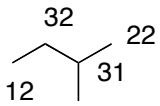
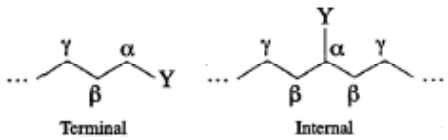
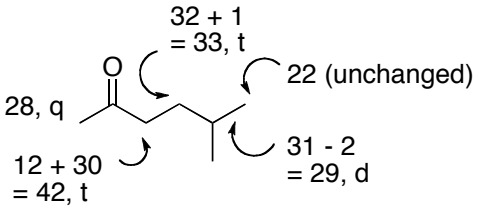


Table C.11 Incremental Substituent Effects (ppm) on Replacement of H by Y in Alkanes



	α		β		γ
Y	TERMINAL	INTERNAL	TERMINAL	INTERNAL	
CH_3	+ 9	+ 9	+ 6	+ 6	−2
$CH=CH_2$	+20		+ 6		−0.5
C CH	+ 4.5		+ 5.5		−3.5
COOH	+21	+16	+3	+ 2	−2
COO^-	+25	+20	+5	+ 3	−2
COOR	+20	+17	+3	+ 2	−2
COCl	+33	28		+ 2	
$CONH_2$	+22		+ 2.5		−0.5
COR	+30	+24	+ 1	+ 1	−2
CHO	+31		0		−2
Phenyl	+23	+17	+ 9	+ 7	−2
OH	+48	+41	+10	+ 8	−5
OR	+58	+51	+ 8	+ 5	−4
OCOR	+51	+45	+ 6	+ 5	−3
NH_2	+29	+24	+11	+10	−5
NH_3	+26	+24	+ 8	+ 6	−5
NHR	+37	+31	+ 8	+ 6	−4
NR_2	+42		+ 6		−3
NR_3	+31		+ 5		−7
NO_2	+63	+57	+ 4	+ 4	
CN	+ 4	+ 1	+ 3	+ 3	−3
SH	+11	+11	+12	+11	−4
SR	+20		+ 7		−3
F	+68	+63	+ 9	+ 6	−4
Cl	+31	+32	+11	+10	−4
Br	+20	+25	+11	+10	−3
I	− 6	+ 4	+11	+12	−1

We add the appropriate and α, β, and γ shifts from Table C11 to the data from Table C10 to calculate the more precise ^{13}C chemical shifts.



There are problems in this text where you will not be able to choose between two competing solutions until you calculate the "precise" chemical shifts and compare the data for each of the two possible structures to the data for the unknown. To make the comparison, it is useful to put the data in table form. To illustrate, we can compare our calculated chemical shifts with those actually observed.

Calculated	**Actual**
22, q (2)	23, q (2)
29, d	28, d
28, q	29, q
33, t	33, t
42, t	42, t

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