



## CHEMISTRY HONOURS EXAMINATION: JUNE 2017

### MODULE: CEM 8X04- INSTRUMENTAL ANALYSIS

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**Moderator:** Dr R. Mampa (University of Limpopo)

### INSTRUCTIONS

- (i) This examination is out of a Total of 100 Marks and you have 3 Hours (180 Minutes) to complete it. No extra time will be allowed for any reason.
- (ii) The Exam comprises 2 Sections. PLEASE ANSWER EACH SECTION IN A SEPARATE BOOK.
- (iii) The use of cell phones and other electronic devices is forbidden and they must be switched off.

### SECTION 1: NMR, IR, MS and UV-VIS SPECTROSCOPY

#### QUESTION 1

(52)

The following spectroscopic data is for a compound of molecular formula  $C_{10}H_{11}BrO$ .

**$^1H$  NMR (300 MHz;  $CDCl_3$ ;  $Me_4Si$ )**  $\delta$  7.78, doublet,  $J = 7.5$  Hz, integration = 2H, 7.51, doublet,  $J = 7.5$  Hz, integration = 2H, 2.55, triplet,  $J = 7.0$  Hz, integration = 2H, 1.52, sextet,  $J = 7.0$  Hz, integration = 2H, 0.96, triplet,  $J = 7.0$  Hz, integration = 3H.

**$^{13}C$  NMR (75 MHz;  $CDCl_3$ ) & DEPT**  $\delta$  197.6 (C), 136.4 (C), 131.7 (CH), 130.8 (CH), 127.5 (C), 41.3 ( $CH_2$ ), 17.2 ( $CH_2$ ), 13.5 ( $CH_3$ ).

**$\nu_{max}(\text{film})/cm^{-1}$ :** 3078m, 2962m, 1690s, 1594m, 1465m, and 1375m.

**$m/z$ :** 226 (100.0%), 228 (97.3%), 183 (51%), 185 (49%), 147 (79%), 197 (51%) 199 (41%), 186 (34%) and 184 (37%).

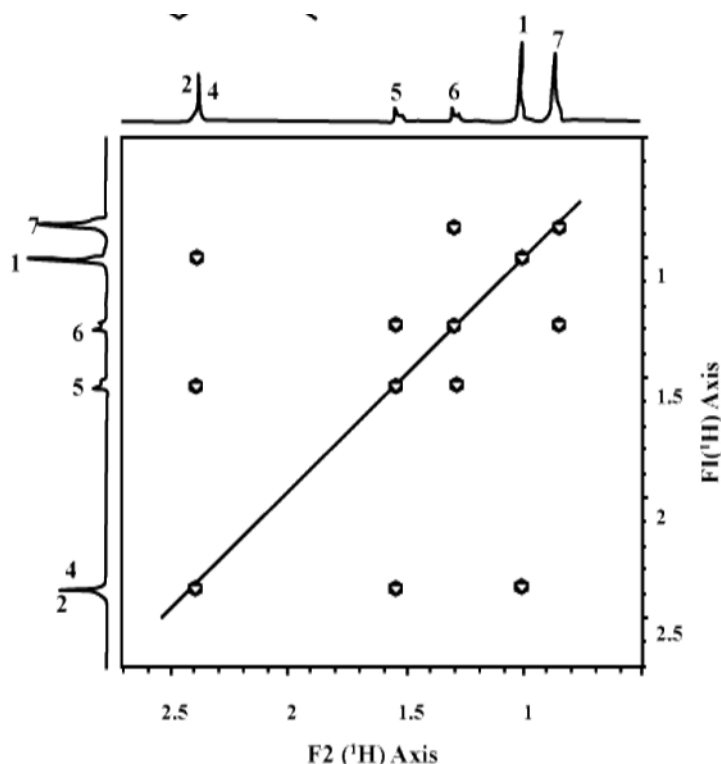
- 1.1:** Decipher the structure of the above compound, succinctly outlining your reasoning. Make sure that you assign each IR peak to a specific type of bond vibration in the structure (15)
- 1.2:** Assign each proton signal and each carbon signal to a specific atom in the structure. (12)
- 1.3:** Do the relevant calculations to confirm your  $^1H$  and  $^{13}C$  assignments. (6)
- 1.4:** In the mass spectral data:

- (a) Most of the peaks appear as doublets of nearly the same intensity. Why is that the case? (2)
- (b) Give the fragments that give rise to the peaks at 226 and 228. (2)
- (c) Show how the fragments at 183 and 185 come about. (4)
- (d) Show how the fragment at 147 comes about. (3)
- (e) The two sets of fragments at 197 & 199, and those at 184 & 186 result from McLafferty rearrangement to the carbonyl and to the aromatic ring respectively. Show how these occur. (8)

## QUESTION 2

(14)

The following is a simulated COSY spectrum of heptanone. Please answer the questions that follow.

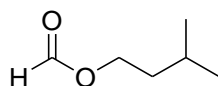


- 2.1 Which isomer of heptanone is this a spectrum of? Please give a reason for your answer. (2)
- 2.2 How would you use DEPT Spectra to confirm your answer above? (4)
- 2.3 Predict the splitting pattern/multiplicity of the peaks numbered 1, 2, 4, 5, 6 and 7, as well as the expected coupling constants. (4)
- 2.4 Explain in details, how the depicted spectrum confirms your answer to 2.1 above. (4)

## QUESTION 3

(6)

Draw a simulated heteronuclear single quantum coherence (HSQC) spectrum of isobutyl formate. The two axes must be drawn to scale, with signal multiplicities correctly reflected on the proton spectral axis.



## SECTION 2: SURFACE CHARACTERIZATION TECHNIQUES

**PLEASE ADD QUESTIONS HERE FOR 28 MARKS**

### QUESTION 4

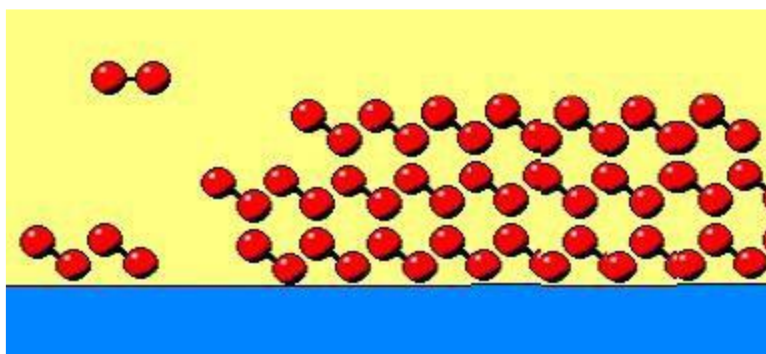
**(15)**

4.1. Explain the formation of hysteresis loop in the type IV isotherm. Use diagram(s) where necessary. **(2)**

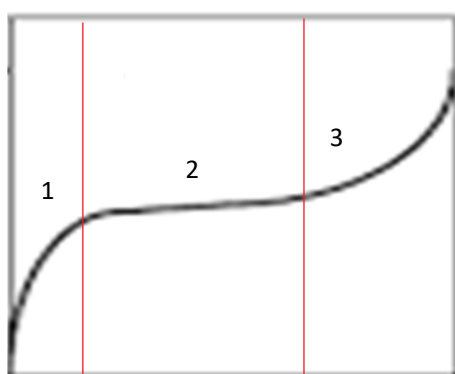
4.2. How will the adsorption isotherm look like if a material is only microporous and give reasons? **(2)**

4.3. Derive the BET equation from first principle. **(5)**

4.4. From the diagram shown below, which of the Langmuir assumptions do not hold true? **(2)**



4.5. Explain regions I, II and III in the type II isotherm shown below in terms of adsorption. Determine and briefly explain where you are most likely to get reliable surface area information in this isotherm. **(4)**

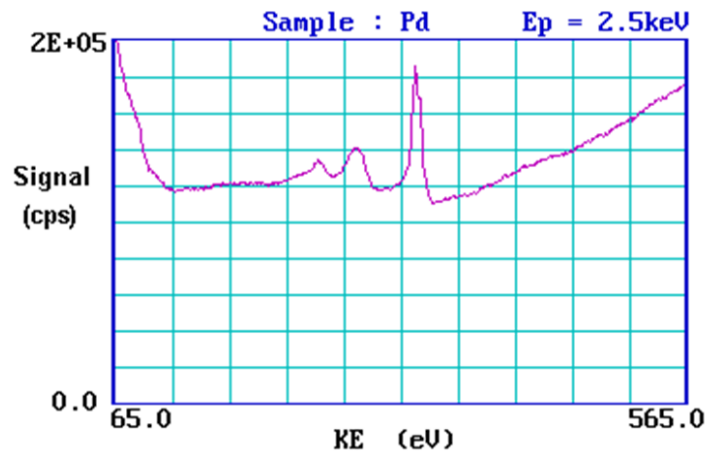


## QUESTION 5

(5)

5.1. Explain the working principle of the two electron spectroscopes (Use diagrams where necessary). (3)

5.2. Identify the spectrum below as either XPS or AES and explain the increase in signal intensity at high kinetic energies. (2)



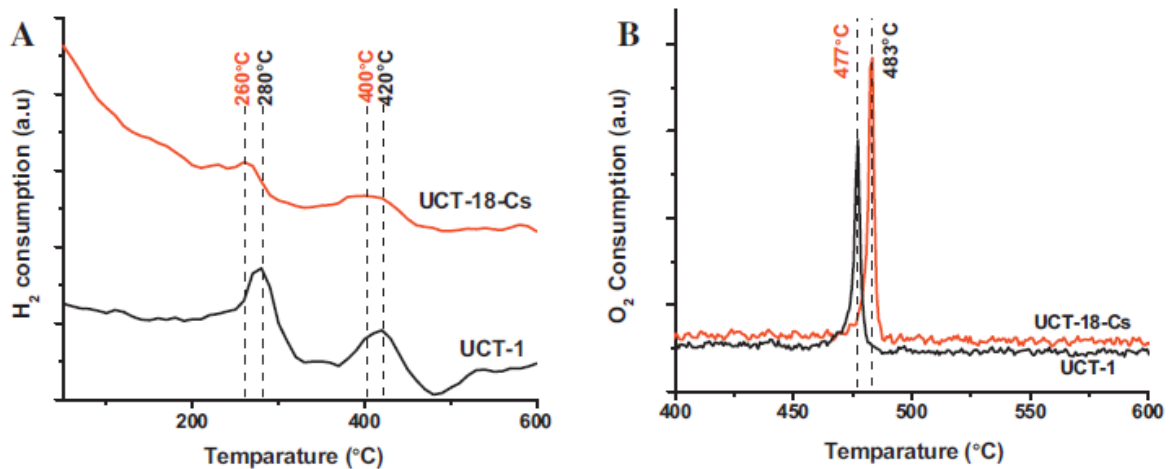
## QUESTION 6

(5)

6.1. UCT-1 and UCT-18 are mesoporous manganese oxide and Cs-doped mesoporous manganese oxide, respectively.

6.1.1. Which graph best represents  $O_2$ -TPO? (1)

6.1.2. If the mesoporous manganese oxide has a ratio of Mn:O of 2:3, assign the reduction profile of UCT-1 and comment of the effect of doping with Cs (4)



## QUESTION 7

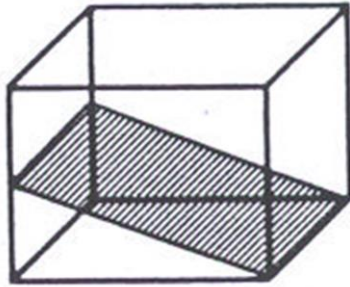
7.1. Define Bragg's law

(1)

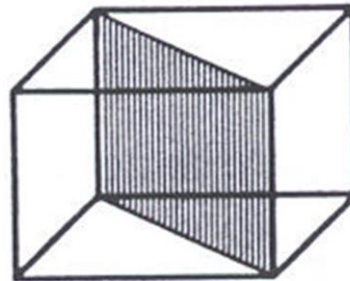
7.2. Give fractional intercepts (where appropriate) and Miller indices of the simple cubic systems given below.

(2)

A



B



**Table of Characteristic IR Absorptions**

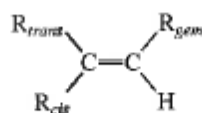
<i>frequency, cm<sup>-1</sup></i>	<i>bond</i>	<i>functional group</i>
3640–3610 (s, sh)	O–H stretch, free hydroxyl	alcohols, phenols
3500–3200 (s,b)	O–H stretch, H-bonded	alcohols, phenols
3400–3250 (m)	N–H stretch	1°, 2° amines, amides
3300–2500 (m)	O–H stretch	carboxylic acids
3330–3270 (n, s)	–C≡C–H: C–H stretch	alkynes (terminal)
3100–3000 (s)	C–H stretch	aromatics
3100–3000 (m)	=C–H stretch	alkenes
3000–2850 (m)	C–H stretch	alkanes
2830–2695 (m)	H–C=O: C–H stretch	aldehydes
2260–2210 (v)	C≡N stretch	nitriles
2260–2100 (w)	–C≡C– stretch	alkynes
1760–1665 (s)	C=O stretch	carbonyls (general)
1760–1690 (s)	C=O stretch	carboxylic acids
1750–1735 (s)	C=O stretch	esters, saturated aliphatic
1740–1720 (s)	C=O stretch	aldehydes, saturated aliphatic
1730–1715 (s)	C=O stretch	α, β-unsaturated esters
1715 (s)	C=O stretch	ketones, saturated aliphatic
1710–1665 (s)	C=O stretch	α, β-unsaturated aldehydes, ketones
1680–1640 (m)	–C=C– stretch	alkenes
1650–1580 (m)	N–H bend	1° amines
1600–1585 (m)	C–C stretch (in-ring)	aromatics
1550–1475 (s)	N–O asymmetric stretch	nitro compounds
1500–1400 (m)	C–C stretch (in-ring)	aromatics
1470–1450 (m)	C–H bend	alkanes
1370–1350 (m)	C–H rock	alkanes
1360–1290 (m)	N–O symmetric stretch	nitro compounds
1335–1250 (s)	C–N stretch	aromatic amines
1320–1000 (s)	C–O stretch	alcohols, carboxylic acids, esters, ethers
1300–1150 (m)	C–H wag (–CH <sub>2</sub> X)	alkyl halides
1250–1020 (m)	C–N stretch	aliphatic amines
1000–650 (s)	=C–H bend	alkenes
950–910 (m)	O–H bend	carboxylic acids
910–665 (s, b)	N–H wag	1°, 2° amines
900–675 (s)	C–H “oop”	aromatics
850–550 (m)	C–Cl stretch	alkyl halides
725–720 (m)	C–H rock	alkanes
700–610 (b, s)	–C≡C–H: C–H bend	alkynes
690–515 (m)	C–Br stretch	alkyl halides

m=medium, w=weak, s=strong, n=narrow, b=broad, sh=sharp

# <sup>1</sup>H NMR Correlation Chart



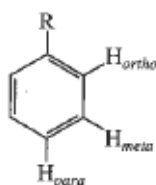
## <sup>1</sup>H CHEMICAL-SHIFT CALCULATIONS FOR SUBSTITUTED ALKENES



$$\delta_{\text{H}} \text{ ppm} = 5.25 + \delta_{\text{gem}} + \delta_{\text{cis}} + \delta_{\text{trans}}$$

Substituents (–R)	$\delta_{\text{gem}}$	$\delta_{\text{cis}}$	$\delta_{\text{trans}}$
Saturated carbon groups			
Alkyl	0.44	–0.26	–0.29
–CH <sub>2</sub> –O–	0.67	–0.02	–0.07
Aromatic groups			
–C <sub>6</sub> H <sub>5</sub>	1.35	0.37	–0.10
Carbonyl, acid derivatives, and nitrile			
COR	1.10	1.13	0.81
–COOH	1.00	1.35	0.74
–COOR	0.84	1.15	0.56
–C≡N	0.23	0.78	0.58
Oxygen groups			
–OR	1.18	–1.06	–1.28
–OCOR	2.09	–0.40	–0.67
Nitrogen groups			
–NR <sub>2</sub>	0.80	–1.26	–1.21
–NO <sub>2</sub>	1.87	1.30	0.62
Halogen groups			
–F	1.54	–0.40	–1.02
–Cl	1.08	0.19	0.13
–Br	1.04	0.40	0.55
–I	1.14	0.81	0.88

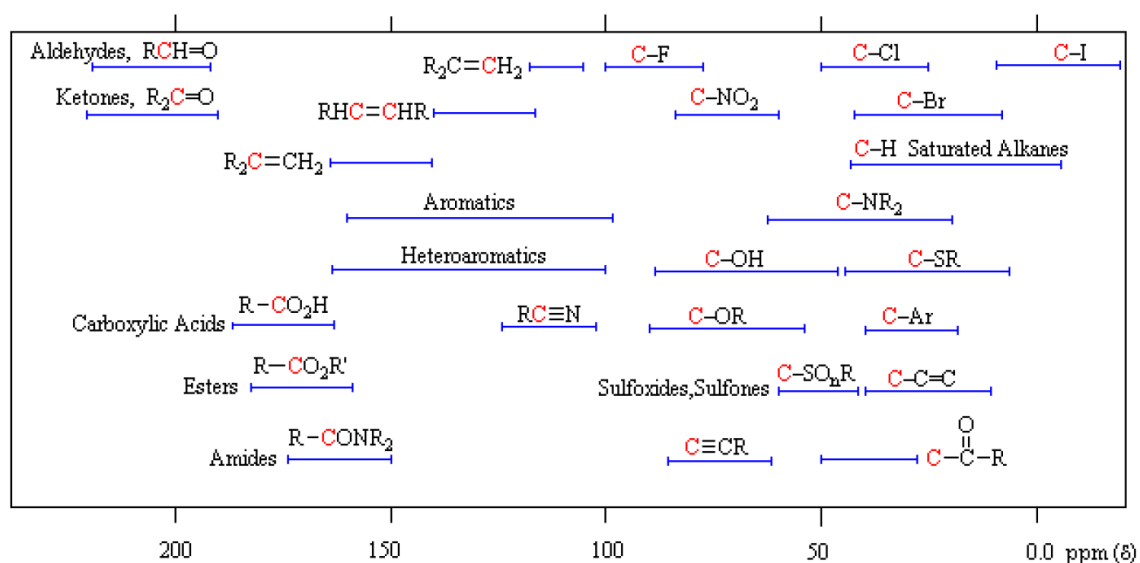
# <sup>1</sup>H CHEMICAL-SHIFT CALCULATIONS FOR SUBSTITUTED BENZENE RINGS



$$\delta_H \text{ ppm} = 7.27 + \Sigma \delta$$

Substituents (-R)	$\delta_{ortho}$	$\delta_{meta}$	$\delta_{para}$
<b>Saturated carbon groups</b>			
Alkyl	-0.14	-0.06	-0.17
-CH <sub>2</sub> OH	-0.07	-0.07	-0.07
<b>Aldehydes and ketones</b>			
-CHO	0.61	0.25	0.35
-COR	0.62	0.14	0.21
<b>Carboxylic acids and derivatives</b>			
-COOH	0.85	0.18	0.34
-COOR	0.71	0.10	0.21
-C≡N	0.25	0.18	0.30
<b>Oxygen groups</b>			
-OH	-0.53	-0.17	-0.45
-OCH <sub>3</sub>	-0.48	-0.09	-0.44
-OCOCH <sub>3</sub>	-0.19	-0.03	-0.19
<b>Nitrogen groups</b>			
-NH <sub>2</sub>	-0.80	-0.25	-0.65
-NO <sub>2</sub>	0.95	0.26	0.38
<b>Halogen groups</b>			
-F	-0.29	-0.02	-0.23
-Cl	0.03	-0.02	-0.09
-Br	0.18	-0.08	-0.04
-I	0.38	-0.23	-0.01

## <sup>13</sup>C NMR Correlation Chart





<sup>13</sup>C SUBSTITUENT INCREMENTS FOR ALKENE (VINYL) CARBONS<sup>a,b</sup>

$\begin{array}{c} \gamma-\beta-\alpha \\ \quad \diagdown \quad \diagup \\ \quad \text{C}=\text{C} \\ \quad \diagup \quad \diagdown \\ \alpha' \quad \beta'-\gamma' \end{array}$						
Substituent	$\alpha$	$\beta$	$\gamma$	$\alpha'$	$\beta'$	$\gamma'$
Carbon	10.6	7.2	-1.5	-7.9	-1.8	-1.5
-C <sub>6</sub> H <sub>5</sub>	12			-11		
-OR	29	2		-39	-1	
-OCOR	18			-27		
-COR	15			6		
-COOH	4			9		
-CN	-16			15		
-Cl	3	-1		-6	2	
-Br	-8	0		-1	2	
-I	-38			7		

<sup>a</sup>In the upper chains, if a group is in the  $\beta$  or  $\gamma$  position, the preceding atoms ( $\alpha$  and/or  $\beta$ ) are assumed to be carbon atoms. Add these increments to the base value of ethylene (123.3 ppm).

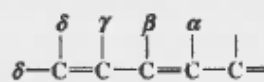
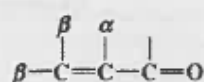
<sup>b</sup>Calculate C1 as shown in the diagram. Redefine C2 as C1 when estimating values for C2.

<sup>13</sup>C SUBSTITUENT INCREMENTS FOR BENZENE RINGS (PPM)<sup>a</sup>

Substituent Y	$\alpha$ (ipso)	$o$ (ortho)	$m$ (meta)	$p$ (para)
-CH <sub>3</sub>	9.3	0.7	-0.1	-2.9
-CH <sub>2</sub> CH <sub>3</sub>	11.7	-0.5	0	-2.6
-CH(CH <sub>2</sub> ) <sub>2</sub>	20.1	-2.0	-0.3	-2.5
-C(CH <sub>3</sub> ) <sub>3</sub>	18.6	-3.4	-0.4	-3.1
-CH=CH <sub>2</sub>	9.1	-2.4	0.2	-0.5
-C=CH	-6.2	3.6	-0.4	-0.3
-C <sub>6</sub> H <sub>5</sub>	8.1	-1.1	-0.5	-1.1
-CHO	8.2	1.2	0.6	5.8
-COCH <sub>3</sub>	8.9	-0.1	-0.1	4.4
-COC <sub>6</sub> H <sub>5</sub>	9.1	1.5	-0.2	3.8
-COOH	2.1	1.6	-0.1	5.2
-COOCH <sub>3</sub>	2.0	1.2	-0.1	4.3
-CN	-16.0	3.6	0.6	4.3
-NH <sub>2</sub>	18.2	-13.4	0.8	-10.0
-N(CH <sub>3</sub> ) <sub>2</sub>	16.0	-15.7	0.8	-10.5
-NHCOCH <sub>3</sub>	9.7	-8.1	0.2	-4.4
-NO <sub>2</sub>	19.6	-4.9	0.9	6.0
-OH	28.8	-12.7	1.6	-7.3
-OCH <sub>3</sub>	33.5	-14.4	1.0	-7.7
-OCOCH <sub>3</sub>	22.4	-7.1	-0.4	-3.2
-F	33.6	-13.0	1.6	-4.5
-Cl	5.3	0.4	1.4	-1.9
-Br	-5.4	3.4	2.2	-1.0
-I	-31.2	8.9	1.6	-1.1

<sup>a</sup>Add these increments to the base value for benzene-ring carbons (128.5 ppm).

### EMPIRICAL RULES FOR ENONES



Base values:

Six-membered ring or acyclic parent enone	= 215 nm
Five-membered ring parent enone	= 202 nm
Acyclic dienone	= 245 nm

Increments for:

Double-bond-extending conjugation	30
Alkyl group or ring residue	$\alpha$ 10
	$\beta$ 12
	$\gamma$ and higher 18

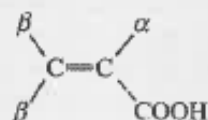
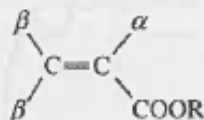
Polar groupings:

-OH	$\alpha$ 35
	$\beta$ 30
	$\delta$ 50
-OCOCH <sub>3</sub>	$\alpha, \beta, \delta$ 6
-OCH <sub>3</sub>	$\alpha$ 35
	$\beta$ 30
	$\gamma$ 17
	$\delta$ 31
-Cl	$\alpha$ 15
	$\beta$ 12
-Br	$\alpha$ 25
	$\beta$ 30
-NR <sub>2</sub>	$\beta$ 95
Exocyclic double bond	5
Homocyclic diene component	39
Solvent correction	Variable

$$\lambda_{\text{max}}^{\text{EtOH}} (\text{calc}) = \text{Total}$$

### EMPIRICAL RULES FOR UNSATURATED ACIDS AND ESTERS

Base values for:



With $\alpha$ or $\beta$ alkyl group	208 nm
With $\alpha, \beta$ or $\beta, \beta$ alkyl groups	217
With $\alpha, \beta, \beta$ alkyl groups	225
For an exocyclic $\alpha, \beta$ double bond	Add 5 nm
For an endocyclic $\alpha, \beta$ double bond in a five- or seven-membered ring	Add 5 nm