系所組別：生物化學暨分子生物學研究所甲，乙組
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## 1－44（2 points for each）and 45 （ 12 points）

## 請勿在本試敬紙上作答，否則不予計分

1．Rank the labeled protons in the following compound in order of increasing acidity．

a） $\mathrm{Ha}<\mathrm{Hb}<\mathrm{Hc}$
b） $\mathrm{Hc}<\mathrm{Ha}<\mathrm{Hb}$ ．
c） $\mathrm{Ha}<\mathrm{Hc}<\mathrm{Hb}$ ．
d） $\mathrm{Hc}<\mathrm{Hb}<\mathrm{Ha}$
e） $\mathrm{Hb}<\mathrm{Hc}<\mathrm{Ha}$ ．

2．Which alkyl halide is used to prepare $\mathrm{CH}_{3} \mathrm{OCH}_{2} \mathrm{CH}_{2} \mathrm{CO}_{2} \mathrm{H}$ by a malonic ester synthesis？
a） $\mathrm{CH}_{3}$
b） $\mathrm{CH}_{3} \mathrm{OCH}_{2} \mathrm{Br}$
c） $\mathrm{CH}_{3} \mathrm{OCH}_{2} \mathrm{CH}_{2} \mathrm{Br}$
d） $\mathrm{BrCH}_{2} \mathrm{CO}_{2} \mathrm{H}$
e） $\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{Br}$

3．Which base converts diisopropylamine quantitatively into lithium diisopropylamide
a） BuLi
b） LiOH
c） $\mathrm{LiOCH}_{2} \mathrm{CH}_{3}$
d） $\mathrm{LiOCH}_{2} \mathrm{CH}_{3}$
e） $\mathrm{LiO}-t-\mathrm{Bu}$

4．What diester gives the following product by a Dieckmann reaction？

a）diethyl malonate
b）diethyl hexanedioate
c）diethyl succinate
d）diethyl heptanedioate
e）diethyl hexanedioate

5．Rank the compounds in the box in order of increasing basicity．

A

B

C
a） A $<$ B $<$ C
b） B $<$ C $<$ A
c） B $<$ C $<$ A
d） A $<$ C $<$ B
e） C $<$ A $<$ B
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6．Which alkyl halide is used to prepare 2－pentanone by an acetoacetic ester synthesis？
a） $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{Br}$
b） $\mathrm{CH}_{3} \mathrm{I}$
c） $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{Br}$
d） $\mathrm{CH}_{3} \mathrm{COCH}_{2} \mathrm{Br}$
e） $\mathrm{BrCH}_{2} \mathrm{COCH}_{3}$

7．Which amongst A－D is the best alternative resonance structure for structure X ？


X

B


C


D
a） A
b）B
c） C
d）D
e）None of them

8．What is the correct IUPAC name for the following structure？

a）3－isopropyl－4－methylhexane
b）4－isopropyl－2－methylhexane
c）2，5－dimethyl－4－ethylheptane
d）4－ethyl－3，6－dimethylheptane
e）None of them

9．Circle the compound shown below that is likely to have a dipole moment of zero．
a） $\mathrm{CHCl}_{3}$
b） $\mathrm{CF}_{4}$
c） $\mathrm{CF}_{3} \mathrm{CHF}_{2}$
d） $\mathrm{CH}_{2}=\mathrm{CCl}_{2}$
e） $\mathrm{CH}_{2} \mathrm{I}_{2}$

10．Which statement about cis－1－butyl－2－methylcyclohexane is not true？
a）The butyl group can occupy an equatorial position in an energy minimum chair conformer
b）The methyl group can occupy an equatorial position in an energy minimum chair conformer
c）The methyl and butyl groups will occupy equatorial positions at the same time in an energy minimum chair conformer
d）One of its energy minimum chair conformers will have an alkyl group in an axial position
e）One of its energy minimum chair conformers will have an alkyl group in an equatorial position

11．Which compound will have the largest equilibrium difference in concentration between its two chair conformational isomers at room temperature？
a）tert－butylcyclohexane
b）propylcyclohexane
c）methylcyclohexane
d）ethylcyclohexane
e）cyclohexane
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12．The following reaction is which general type？

a）substitution reaction
b）addition reaction
c）rearrangement reaction
d）elimination reaction
e）redox reaction

13．What is the correct name for the molecule shown below？



H points inward at $\mathrm{C}-3$ （since Br points outward） C 3 is R

$H$ points outward at $\mathrm{C}-4$ （since $\mathrm{CH}_{3}$ points inward） so＂reverse＂meaning of curved arrow C 4 is S
a．（3S，4R）－3－bromo－4－methylheptane
b．（3S，4S）－4－bromo－3－methylheptane
c．（3R，4R）－3－bromo－4－methylheptane
d．$(3 \mathrm{R}, 4 \mathrm{~S})$－3－bromo－4－methylheptane
e．（3R，4R）－4－bromo－3－methylheptane
14．Which set of reactions will carry out the transformation shown below？

（a）（i）concentrated HBr ，then（ii） Mg in dry ether，then（iii）water
（b）（i） $\mathrm{PCl}_{3}$ ，then（ii） Mg in dry ether，then（iii）water
（c）（i） 1 equiv of $\mathrm{Br}_{2}$ ，then（ii） 4 equiv of $\mathrm{NaNH}_{2}$
（d）（i） $\mathrm{LiAlH}_{4}$ in dry ether，then（iii）water
（e）None of them
15．For the reaction that is shown，which statement is most likely to be true？

$\xrightarrow{\text { dimethylsulioxide }}$
（a polar，aprotic solvent）

A

8
（a）the reaction rate will depend only upon the concentration of KOH
（b）the product B is expected to form in highest yield
（c）the reaction rate will depend only upon the concentration of the alkyl bromide
（d）the products A and B are expected to form in similar（not necessarily equal）yields
（e）the reaction rate will depend upon the concentrations of both the alkyl bromide and KOH
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16．（R）－2－Chloropentane has a specific rotation of $[\alpha] \mathrm{D}=+46.5^{\circ}$ at room temperature．Treat it with 1 equiv of KI in a nonreactive solvent，isolate the product，then treat this first product with KCl ．What do you expect to be the specific rotation of the final product from these two reactions？

（a）$[\alpha] \mathrm{D}=-46.5^{\circ}$
（b）$[\alpha] \mathrm{D}=+46.5^{\circ}$
（c）$[\alpha] \mathrm{D}=0^{\circ}$（no optical rotation）
（d）$[\alpha] \mathrm{D}=-23.25^{\circ}$
（e）$[\alpha] \mathrm{D}=+23.25^{\circ}$

17－24．Monosaccharides can be depicted by a variety of different structural representations．On the followings are structures for eight monosaccharides．Match each of the descriptions that follow with the letter of the corresponding structural formula．Note that a letter may be used more than once or not at all．

A

B

c

0

E

F

G

H

17．a glycoside $\qquad$
18．an aldopentose $\qquad$
19．an aldonic acid $\qquad$
20．a pair of enantiomers $\qquad$ and $\qquad$
21．a furanose $\qquad$
22．two representations of D－glucose $\qquad$ and $\qquad$
23．an L－sugar $\qquad$
24．two compounds that form the same phenylosazone derivative $\qquad$ and $\qquad$
25．The compound below is treated with 1 equivalent of $\mathrm{Br}_{2}$ in the presence of a bright light．At which position do expect reaction in greatest amount under these conditions．

（a） 1
（b） 2 or 5
（c） 3 or 4
（d） Me
（e） 2 or 3

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26．Which statement below is not true？
（a）3－hexyne is more stable than 1－hexyne
（b）1－hexyne can be deprotonated by $\mathrm{KNH}_{2}$
（c）1－hexene can be deprotonated by $\mathrm{NaNH}_{2}$
（d）Cyclopentyne is unlikely to be able to be isolated at room temperature
（e）Hexane is more stable than hexyne．

27．Which＂name reaction＂can be used to alkylate a carbonyl compound？
（a）aldol reaction
（b）enamine synthesis
（c）haloform reaction
（d）Baeyer－Villiger reaction
（e）condensation reaction

28．The pKa of benzoic acid is 4.05 ．Which statement correctly describes the structure of benzoic acid at different pH ＇s？
（a）At pH 10 benzoic acid is completely protonated．
（b）At pH 4 ，benzoic acid is roughly $50 \%$ dissociated into the benzoate anion．
（c）At pH 1 benzoic acid exists exclusively as the benzoate anion．
（d）All of the above．
（e）None of them

29．Which compound cannot be converted to a carboxylic acid by hydrolysis？
（a）Aldehyde
（b）Amide
（c）Anhydride
（d）Ester
（e）All of them

30．Which reagent will reduce a carbonyl compound to an alcohol？
（a） OH －（aq）
（b） $\mathrm{Zn}(\mathrm{Hg}), \mathrm{HCl}$ ，heat
（c）LDA
（d） $\mathrm{LiAlH}_{4}$
（e） NaOH

31．Which term accurately describes the properties of an enolate anion？
（a）strong base
（b）powerful nucleophile
（c）weak acid
（d）Both A and B
（e）None of them

32．What is the product of the reaction of a Grignard reagent with dry ice $\left[\mathrm{CO}_{2}(\mathrm{~s})\right]$ ？
（a）primary alcohol
（b）aldehyde
（c）carboxylic acid
（d）ester
（e）amine

33．The $\mathrm{p} K_{\mathrm{a}}$ of propanoic acid is about 4．7．Estimate the $\mathrm{p} K \mathrm{a}$ of 2－chloropropanoic acid．
（a）$<4.7$
（b） 4.7
（c）$>4.7$
（d）None of them
（e）Impossible to determine without a pH meter．

34．Which term best describes the twelve protons of TMS？
（a）Highly shielded
（b）Deshielded
（c）Downfield
（d）Nonequivalent
（e）None of them

## 系所組別：生物化學暨分子生物學研究所甲，乙組

考試科目：有機化學
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35．The NMR experiment is carried out in a powerful magnetic field．A certain proton has a chemical shift of 3.20 ppm at 200 MHz ．What is its chemical shift at 400 MHz ？
（a） 1.60 ppm
（b） 3.20 ppm
（c） 6.40 ppm
（d） 9.60 ppm
（e）impossible to determine from the information given

36．What is the total number of aldohexose stereoisomers with the L－configuration？
（a）one
（b）two
（c）four
（d）eight
（e）sixteen

37．The coupling constant，$J$ ，between two adjacent protons is 8 Hz at 200 MHz ．Determine the coupling constant at 400 MHz ．
（a） 4 Hz
（b） 8 Hz
（c） 16 Hz
（d） 32 Hz
（e）impossible to determine from the information given

38．Account for the fact that the mass spectrum of 1－chloropropane $\left(\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{Cl}\right)$ shows peaks at $\mathrm{m} / \mathrm{z}=78$ and 80 ．
（a）Chlorine has two naturally occurring isotopes with masses of 35 and 37 amu ．
（b）1－Chloropropane fragments with loss of the stable molecule $\mathrm{H}_{2}$ ．
（c）1－Chloropropane undergoes a McLafferty rearrangement in the mass spectrometer．
（d）In the mass spectrometer chlorine is converted to ${ }^{78} \mathrm{Br}$ and ${ }^{80} \mathrm{Br}$ ．
（e）None of them

39．Consider the branched hydrocarbon below．Which of the following would NOT be a prominent peak in the mass spectrum of this compound？

（a） $\mathrm{m} / \mathrm{z}=43$
（b）$m / z=57$
（c）$m / z=99$
（d）$m / z=113$
（e）$m / z=155$

40．Why would the Friedel－Crafts alkylation reaction of benzene with 1－chlorobutane be an unsatisfactory method for the synthesis of pure n－butylbenzene？
（a）Unactivated aromatic rings fail to undergo the Friedel－Crafts alkylation reaction．
（b）Primary alkyl chlorides are unreactive in the Friedel－Crafts alkylation reaction．
（c）There is likely to be a skeletal rearrangement，producing a product other than n－butylbenzene．
（d）Friedel－Crafts alkylation of benzene with 1－chlorobutane does produce pure n－butylbenzene．
（e）None of them

41．Which reagent，or combination of reagents，would serve to replace a hydrogen with a halogen atom on an aromatic ring？
（a） $\mathrm{Cl}_{2}, \mathrm{~h} \nu$
（b） $\mathrm{Br}_{2}$ in $\mathrm{CHCl}_{3}$
（c）NBS，$h \nu$
（d） $\mathrm{Cl}_{2}, \mathrm{FeCl}_{3}$
（e）None of them
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42．What would be the product of the electrophilic aromatic substitution reaction to the right？

（a）Aromatic aldehyde
（b）Benzylic chloride
（c）Aromatic ketone
（d）Benzylic alcohol
（e）Benzene

43．What is the result of absorption of UV light by a conjugated diene？
（a）Excitation of an electron from $\pi_{1}$ to $\pi_{2}$ ．
（b）Excitation of an electron from $\pi_{2}$ to $\pi_{3}$ ．
（c）Excitation of an electron from $\pi_{2}$ to $\pi_{4}$ ．
（d）Excitation of an electron from $\pi_{1}$ to $\pi_{3}$ ．
（e）None of them

44．The least reactive carboxylic acid derivatives are characterized by：
（a）A particularly strong carbon－oxygen bond．
（b）An especially weak carbon－oxygen bond．
（c）Extensive $\pi$ electron delocalization．
（d）Both B and C．
（e）None of them

45．Use the NMR data below to identify each of the two unknown organic compounds．
（a） $\mathrm{C}_{5} \mathrm{H}_{10} \mathrm{O}$
${ }^{1}$ H NMR spectrum：（ppm） $2.40(\mathrm{q}, 2 \mathrm{H}), 1.05(\mathrm{t}, 3 \mathrm{H})$
（b） $\mathrm{C}_{8} \mathrm{H}_{10}$

$$
{ }^{13} \mathrm{C} \text { NMR spectrum: (ppm) 21.3, 126.0, 128.1, 129.9, } 137.8
$$

