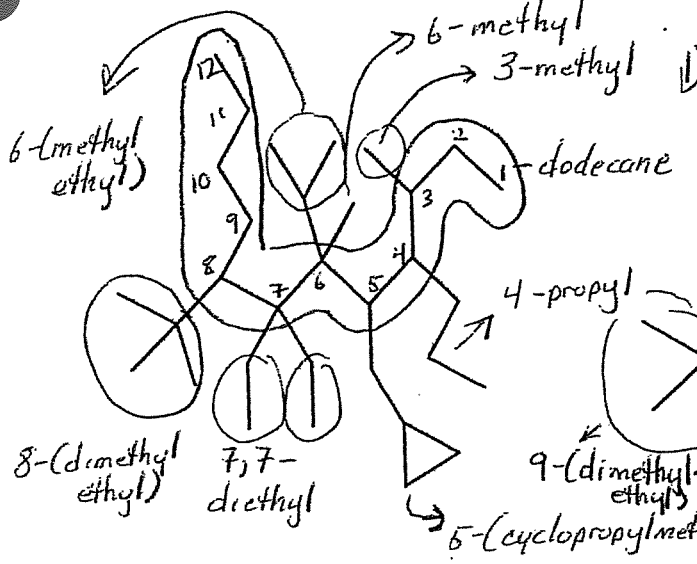
Solutions

Nomenclature Workshop



Problem 1a

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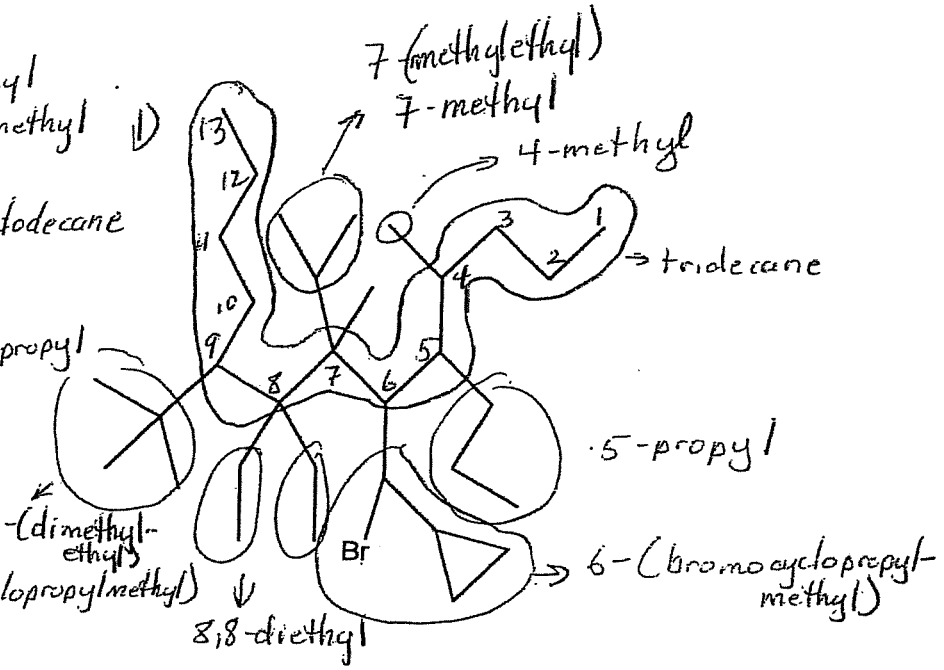
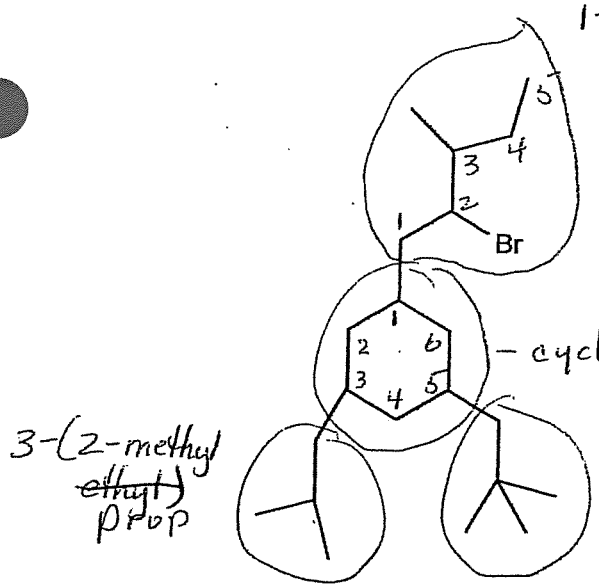


Problem 1b

see link for full name



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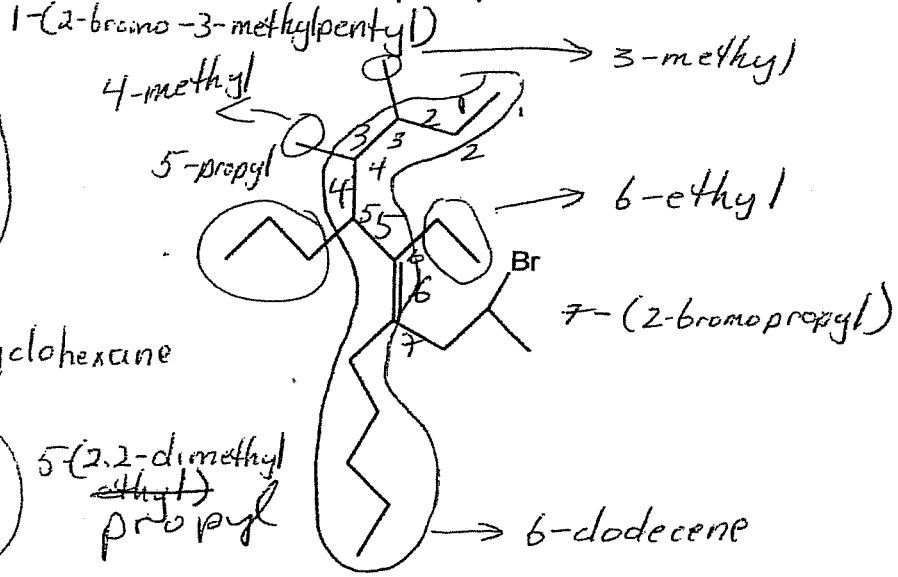

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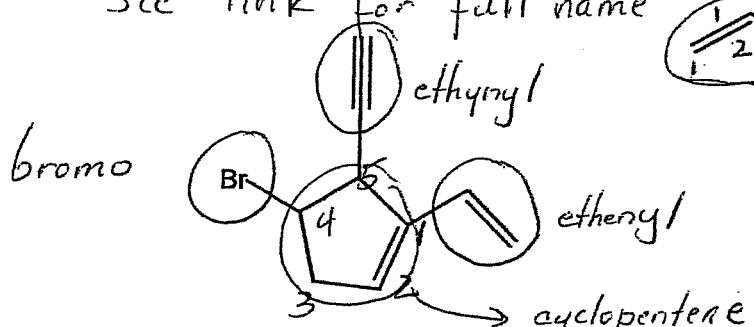

Problem 4

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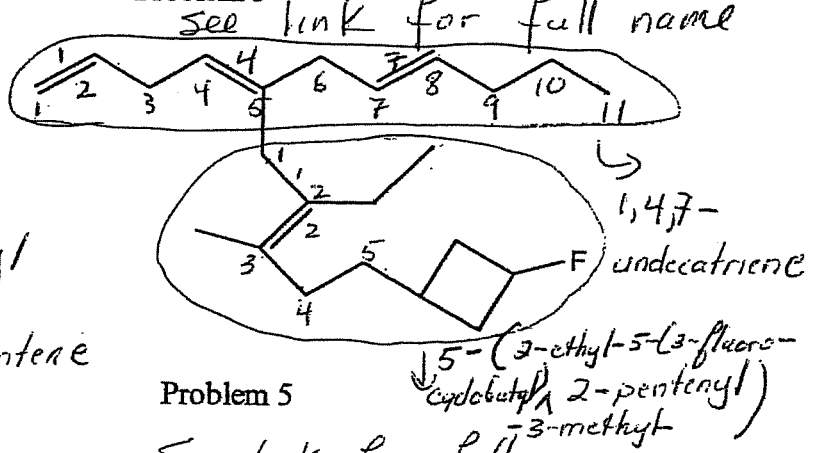

Problem 5

See link for full name

Nomenclature Workshop Solutions

Problem 1a:
5-(cyclopropylmethyl)-7,7-diethyl-6-methyl-6-(methylethyl)-8-(dimethylethyl)-4-(1-methylpropyl)-dodecane

Problem 1b:
6-(bromocyclopropylmethyl)-8,8-diethyl-4,7-dimethyl-7-(methylethyl)-9-(dimethylethyl)-5-propyl-tridecane

Problem 2:

1-(2-bromo-3-methylpentyl)-5-(2,2,-dimethylpropyl)-3-(2-methylpropyl)cyclohexane

Problem 3:

7-(2-bromopropyl)-6-ethyl-3,4-dimethyl-5-propyl-6-dodecene

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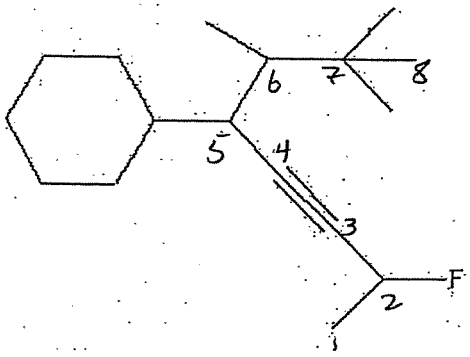
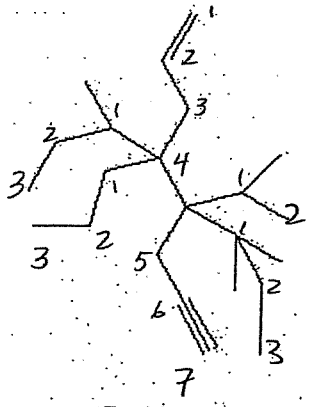
Solutions Nomenclature Workshop - 2



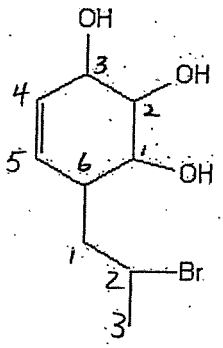
Problem 6

5-cyclohexyl-2-fluoro-6,7-trimethyl-3-octyne



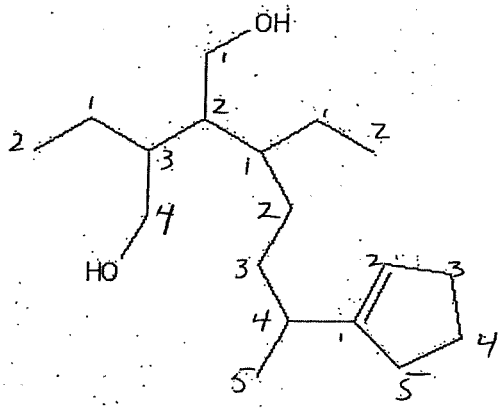
Problem 7

5-(methylethyl)-4(1-methylpropyl)-5-(1,1-dimethylpropyl)-4-propyl-1-octen-7yne



Problem 8

6-(2-bromopropyl)-4-cyclohexene-1,2,3-triol



Problem 9

2-(4-(1-cyclopentenyl)-1-ethyl-pentyl)-3-ethyl-1,4-butanediol

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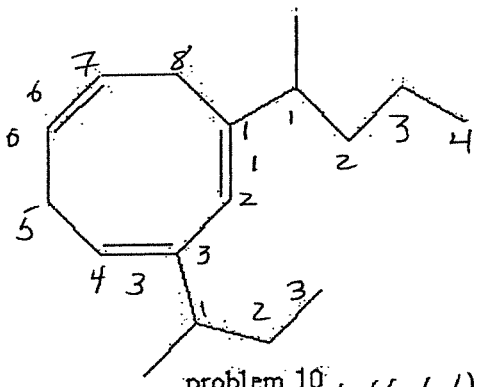
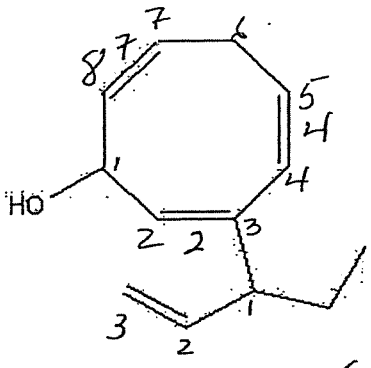
Nomenclature Workshop Continued -3

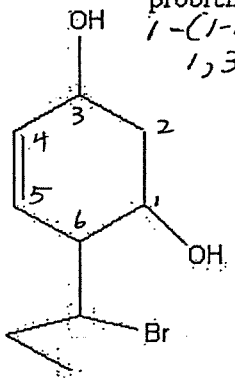
Solutions



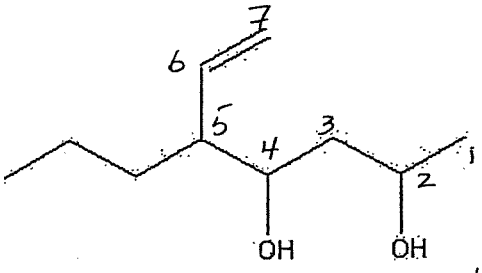
problem 10 1-(1-methylbutyl)-3-(1-methylpropyl)-1,3,6-cyclooctatriene



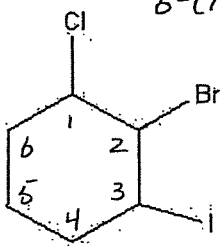
problem 11 3-(1-ethyl-2-propenyl)-2,4,7-cyclooctatrienol



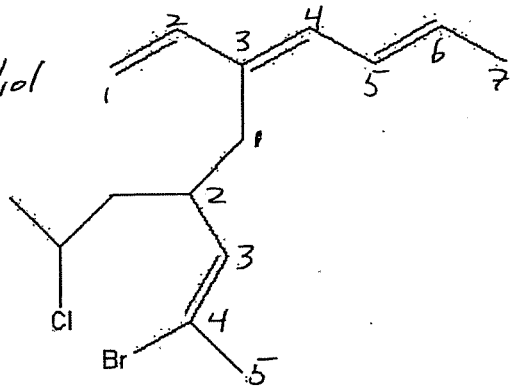
problem 12 6-(1-bromopropyl)-4-cyclohexen-1,3-diol



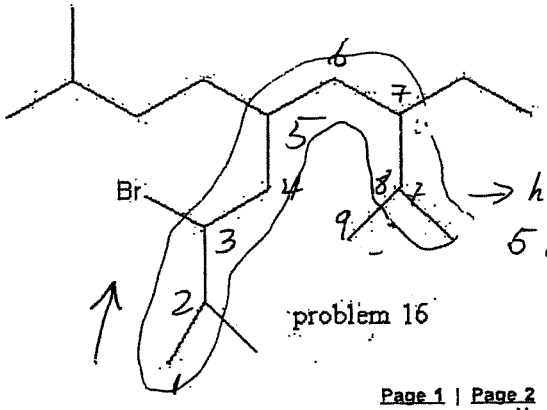
problem 13 5-propyl-6-heptene-2,4-diol



problem 14 2-bromo-1-chloro-3-iodocyclohexane

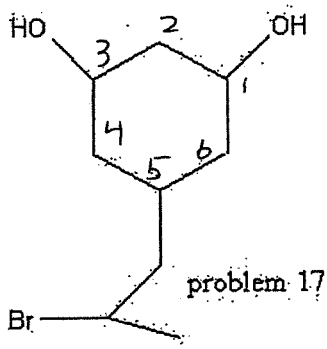


problem 15 3-(4-bromo-2-(2-chloropropyl)-3-pentenyl)-1,3,5-heptatriene



problem 16 3-bromo-7-ethyl-2,9-dimethyl-5-(3-methylbutyl)nonane

has 5 branches



problem 17 5-(2-bromopropyl)-1,3-cyclohexanediol

Amino Acids, Aromatic Compounds, and Carboxylic Acids: How Did They Get Their Common Names?

Sam H. Leung
Department of Chemistry, Washburn University, Topeka, KS 66621; *zzleung@washburn.edu*

Organic chemistry students spend a considerable amount of time learning how to name organic compounds systematically, but they still encounter compounds whose common names are used very often or exclusively. Since the origins of these names are related to the sources, colors, or other unique characteristics of the compounds, it would be interesting to let the students know how some of these names came into existence. Although some textbooks occasionally mention the roots of these names, most of them do not devote a lot of space for this purpose.

Common names are often more interesting than systematic names. Therefore, the derivations of the common names may make learning about the compounds more enjoyable. Articles concerning the origins of the names of the chemical elements have been published in this *Journal* (*1*, *2*). However, a compilation of the name origins of common organic compounds has not appeared. This article provides a survey of the roots of the common names for organic compounds that are most likely to be encountered by undergraduate organic chemistry students. It is not intended to give an in-depth account of the origins but rather a brief look at the roots of the common names. The information, although brief, will allow the students to learn how these compounds got their names. The listings are best used as items of interest and will help lighten up the subject of organic chemistry.

The compounds chosen are divided into three general groups: amino acids (Table 1), aromatic compounds (Table 2), and carboxylic acids (Table 3). Roots of the names and additional notes are given to explain the origin of the common names. Systematic names are included for comparison with the common names and to facilitate structure identification.

Acknowledgments

I would like to thank the reviewers and the Editor of this *Journal* for their valuable suggestions.

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Table 1. Amino Acids

Common Name[a]	Root[b]	Notes	Systematic Name	Ref
Arginine	L *argentum*, silver	forms a well-defined silver salt	(*S*)-2-amino-5-guanidinopentanoic acid	*3*
Asparagine	*asparagus*	first found in asparagus	(*S*)-2-amino-3-carbamoylpropanoic acid	*4, 5*
Aspartic acid	—	related to asparagine	(*S*)-2-aminobutanedioic acid	*5*
Cysteine	—	reduction product of cystine (which see)	(*S*)-2-amino-3-mercaptopropanoic acid	*5*
Cystine	Gk *kystis*, bladder	first isolated from a bladder stone	bis(2-amino-2-carboxyethyl)disulfide	*3*
Glutamic acid	*gluten* + *amino*	obtained by the hydrolysis of gluten, a protein-rich product obtained in the separation of starch from corn or wheat	(*S*)-2-aminopentanedioic acid	*3,*
Glutamine	—	derived from glutamic acid (which see)	(*S*)-2-amino-4-carbamoylbutanoic acid	*6*
Glycine	Gk *glykys*, sweet	tastes sweet	aminoethanoic acid	*3,*
Histidine	Gk *histion*, tissue	—	(*S*)-2-amino-3-(5-imidazolyl)propanoic acid	*6*
Isoleucine	—	isomer of leucine (which see)	(2*S*, 3*S*)-2-amino-3-methylpentanoic acid	*3*
Leucine	Gk *leukos*, white	obtained in the form of white plates	(*S*)-2-amino-4-methylpentanoic acid	
Lysine	Gk *lysis*, loosening	discovered among the products from the hydrolysis of casein	(*S*)-2,6-diaminohexanoic acid	
Methionine	*methyl* + *thio*	contains a S atom [Gk *theion*, sulfur] with a methyl group attached	(*S*)-2-amino-4-methylthiobutanoic acid	
Proline	*pyrrolidine*	contains a pyrrolidine ring	2-pyrrolidinecarboxylic acid	
Serine	L *sericum*, silk	first isolated from silk	(*S*)-2-amino-3-hydroxypropanoic acid	
Threonine	*threose*	spatial configuration analogous to that of D-threose, a 4-carbon sugar	(2*S*,3*R*)-2-amino-3-hydroxybutanoic acid	
Tryptophan	*tryptic* + *phane*	obtained from the pancreatic [tryptic] digestion of proteins: *tryptic*, the adjective form of trypsin, a pancreatic digestive enzyme; phane, from Gk *phanein*, to appear	(*S*)-2-amino-3-(3-indolyl)propanoic acid	
Tyrosine	Gk *tyros*, cheese	found in cheese	(*S*)-2-amino-3-(4-hydroxyphenyl)propanoic acid	
Valine	*valeric*	carbon skeleton corresponds to isovaleric acid (3-methylbutanoic acid)	(*S*)-2-amino-3-methylbutanoic acid	

[a] These biologically important α-amino acids are almost always called by their common names. The suffix *-ine* is a common ending for compounds containing nitrogen (amine bases). [b] L indicates Latin; Gk indicates Greek.

Table 2. Aromatic Compounds

Common Name	Root [a]	Notes	Systematic Name	Ref
Aniline	Sp *añil*, indigo; anil + -ine	first obtained by distillation of indigo; anil is the name for the West Indian shrub *Indigofera suffruticosa*, one of the plants that produce indigo	aminobenzene	*3, 7*
Anisole	Gk *anison*, anise L *ole*, oil	anise is the name of the Egyptian plant *Pimpinella anisum*, which produces aniseed	methoxybenzene	*6*
Anthracene	Gk *anthrax*, coal	a constituent of coal tar	anthracene	*3,*
Catechol	*catechu* + -ol	from gum catechu, an astringent substance obtained from various tropical plants	1,2-dihydroxybenzene	*7*
Cresol (*o*-, *m*-, *p*-)	prob. G *kresol*	from creosote, an oily liquid with a burning, smoky taste, obtained by the distillation of wood tar	1-hydroxy-*x*-methylbenzene [b]	*6*
Cumene		from cumin, a plant native to Egypt and Syria	isopropylbenzene	*5, 6*
Furan	L *furfur*, bran	short for "furfurane"; obtained by decarbonylation of furfural, which was produced by distillation of bran with dilute sulfuric acid	furan	*3, 7*
Hydroquinone		produced by reduction of quinone; first obtained by oxidation of quinic acid	1,4-dihydroxybenzene	*3, 7*
Indole	*indigo*	first obtained by distilling oxindole, a degradation product of indgo, with zinc dust	indole	*7*
Mesitylene		from mesite (Gk *mesos*, between), a liquid whose properties were once thought to be between alcohol and ether and later found to be acetone; mesitylene was so named because it can be made by condensation of three molecules of mesite	1,3,5-trimethylbenzene	*3*
Phenol	phen + -ol; Gk *phaino-*, shining	phene, an old name for benzene; first isolated from illuminating gas in the early 19th century	hydroxybenzene	*7*
Pyridine	Gk *pyro*, fire	obtained by distillation of the oil derived from the pyrolysis of bones	pyridine	*3*
Pyrrole	Gk *pyrro*, fiery red	first detected by the red color produced when its vapor come in contact with pine splinters moistened with concentrated hydrochloric acid	pyrrole	*3, 7*
Resorcinol	*resin* + *orcinol*; It *orcello*, archil	orcinol (3,5-dihydroxytoluene); archil (or orchil) is a violet dye obtained from certain lichens; resorcinol forms when certain resins (from lichen?) are fused with potassium hydroxide	1,3-dihydroxybenzene	*3, 7*
Styrene	L *styrax*, storax	first obtained by distillation of liquid storax, a balsam from *Liquidambar styraciflua* and *Liquidambar orientalis*	ethenylbenzene	*7*
Toluene		obtained by distillation of tolu balsam, a fragrant, yellow-brown resin from the tolu tree, named after the seaport Santiago de Tolú, Colombia	methylbenzene	*3, 5, 6*
Xylene (*o*-, *m*-, *p*-)	.Gk *xylon*, wood	first obtained from wood tar	1,*x*-dimethylbenzene [b]	*3*

[a] Sp indicates Spanish; Gk indicates Greek; L indicates Latin; G indicates German; It indicates Italian. The suffix *-ol* indicates an alcohol.
[b] *x* = 2, 3, or 4.

Table 3. Carboxylic Acids

Common Name [a]	Root [b]	Notes	Systematic Name	Ref
Acetic acid	L *acetum*, vinegar	found in vinegar	ethanoic acid	*3, 8*
Adipic acid	L *adeps*, fat	formed when some unsaturated fats are oxidized	hexanedioic acid	*7*
Butyric acid	L *butyrum*, butter	found in rancid butter	butanoic acid	*3, 4, 8*
Caproic acid	L *caper*, goat	found in goat's milk and has a goatlike odor	hexanoic acid	*3, 4, 8*
Formic acid	L *formica*, ant	was obtained from the destructive distillation of ants	methanoic acid	*3, 8*
Fumaric acid	L *fumus*, smoke	found in the plant *Fumaria*, which was burned in ancient times to create smoke to ward off evil spirits	(*E*)-2-butenedioic acid	*3, 8*
Glutaric acid		first prepared from glutamic acid (an amino acid)	pentanedioic acid	*7*
Lactic acid	L *lac*, milk	first isolated from sour milk	2-hydroxypropanoic acid	*3*
Lauric acid	L *laurus*, laurel		dodecanoic acid	*5*
Linoleic acid	Gk *linon*, flax, + oleic	the flax plant produces long silky fiber used to manufacture linen thread	(*Z,Z*)-9,12-octadecadienoic acid	*6*
Maleic acid	L *malum*, apple	dehydration product of malic acid (which see)	(*Z*)-2-butenedioic acid	*3*
Malic acid	L *malum*, apple	first isolated from unripe apples	hydroxybutanedioic acid	*3, 7*
Malonic acid	L *malum*, apple	first obtained by the oxidation of malic acid (which see)	propanedioic acid	*3, 7*
Oleic acid	L *oleum*, oil	found in the triacylglycerols of some vegetable oils	(*Z*)-9-octadecenoic acid	*3*
Oxalic acid	Gk *oxys*, sharp, sour	has a sharp or sour taste; obtained from plants of the genus *Oxalis*	ethanedioic acid	*3, 9*
Palmitic acid	L *palma*, palm	present in palm oil triacylglycerols	hexadecanoic acid	*3*
Propionic acid	Gk *proto*, first, and *pion*, fat	the smallest acid that shows characteristics of the larger fatty acids	propanoic acid	*3, 4*
Pyruvic acid	Gk *pyro*, fire, and L *uva*, grape	obtained by the pyrolysis of tartaric acid (from grapes)	2-oxopropanoic acid	*3*
Stearic acid	Gk *stear*, tallow	present in the triacylglycerols of animal and vegetable fats	octadecanoic acid	*3*
Succinic acid	L *succinum*, amber	discovered in the distillate from the destructive distillation of amber	butanedioic acid	*3, 8*
Valeric acid		from the root of the plant *Valeriana officinalis*, or garden heliotrope	pentanoic acid	*3, 8*

[a] Although systematic names are becoming more popular, the common names of these monocarboxylic and dicarboxylic acids are still frequently used in organic chemistry and biochemistry. [b] L indicates Latin; Gk indicates Greek.

ON THE ARTIFICIAL PRODUCTION OF UREA

by F. Wöhler

***Annalen der Physik und Chemie,* 88, Leipzig, 1828**

In a brief earlier communication, printed in Volume III of these Annals, I stated that by the action of cyanogen on liquid ammonia, besides several other products, there are formed oxalic acid and a crystallizable white substance, which is certainly not ammonium cyanate, but which one always obtains when one attempts to make ammonium cyanate by combining cyanic acid with ammonia, e.g., by so-called double decomposition. The fact that in the union of these substances they appear to change their nature, and give rise to a new body, drew my attention anew to this subject, and research gave the unexpected result that by the combination of cyanic acid with ammonia, urea is formed, a fact that is noteworthy since it furnishes an example of the artificial production of an organic, indeed a so-called animal substance, from inorganic materials.

I have already stated that the above-mentioned white crystal-line substance is best obtained by breaking down silver cyanate with ammonium chloride solution, or lead cyanate with liquid ammonia. In the latter way I prepared for myself the not unimportant amounts employed in this research. It was precipitated in colourless, transparent crystals, often more than an inch long...

With caustic soda or chalk this substance developed no trace of ammonia; with acids it showed none of the breakdown phenomena of cyanates which occur so easily, namely, the evolution of carbon dioxide and cyanic acid; neither could the lead and silver salts be precipitated from it, as from it, as from a true cyanate; it could thus contain neither cyanic acid nor ammonia as such. Since I found that by the last named method of preparation no other product was formed and the lead oxide was separated in a pure form, I imagined that an organic substance might arise by the union of cyanic acid with ammonia, possibly a substance like a vegetable salifiable base. I therefore made some experiments from this point of view on the behaviour of the crystalline substance to acids. But it was indifferent to them, nitric acid excepted; this, when added to a concentrated solution of the substance, produced at once a precipitate of glistening sales. After these had been purified by several recrystallizations, they showed very acid characters, and I was already inclined to take the compound for a real acid, when I found that after neutralization with bases it gave salts of nitric acid, form which the crystallizable substance could be extracted again with alcohol, with all the characters it had before the addition of nitric acid. This similarity to urea in behaviour induced me to make parallel experiments with perfectly pure urea separated from urine, from which I drew the conclusion that without doubt urea and this crystalline substance, or ammonium cyanate, if one can so call it, are absolutely identical compounds.

I will describe the behaviour of this artificial urea no further, since it coincides perfectly with that of urea from urine, according to the accounts of Proust, Prout and others, to be found in their writings, and I will mention only the fact, not specified by them, that both natural an d artificial urea, on distillation, evolve first large amounts of ammonium carbonate, and then give off to a remarkable extent the stinging, acetic-acid-like smell of cyanic acid, exactly as I found in the distillation of mercuric cyanate or uric acid, and especially of the mercury salt of uric acid. In the distillation of urea, another white, apparently distinct substance also appears, with the examination of which I am still occupied.

But if the combination of cyanic acid and ammonia actually gives urea, it must have exactly the composition allotted to ammonium cyanate by calculation from my composition formula for the cyanates; and this is in fact the case if one atom of water is added to ammonium cyanate, as all ammonium salts contain water, and if Prout's analysis of urea is taken as the most correct. According to him, urea consists of

Nitrogen	46.650	4 atoms
Carbon	19.975	2 atoms
Hydrogen	6.670	8 atoms
Oxygen	26.650	2 atoms
	99.875	

But ammonium cyanate would consist of 56.92 cyanic acid, 28.14 ammonia, and 14.75 water, which for the separate elements gives

Nitrogen	46.78	4 atoms
Carbon	20.19	2 atoms
Hydrogen	6.59	8 atoms
Oxygen	26.24	2 atoms
	99.80	

One would have been able to reckon beforehand that ammonium cyanate with 1 atom of water has the same composition as urea, without having discovered by experiment the formation of urea from cyanic acid and ammonia. By the combustion of cyanic acid with copper oxide one obtains 2 volumes of carbon dioxide and 1 volume of nitrogen, but by the combustion of ammonium cyanate one must obtain equal volumes of these gases, which proportion also holds for urea, as Prout found.

I refrain from the considerations which so naturally offer themselves as a consequence of these facts, e.g., with respect to the composition proportions of organic substances, and the similar elementary and quantitative composition of compounds of very different properties, as for example fulminic acid and cyanic acid, a liquid hydrocarbon and olefiant gas (ethylene). From further experiments on these and similar cases,a general law might be deduced.

tion which treats of "Magnesia Alba" will form the second installment and this will be succeeded by Rutherford's dissertation "On the Air Called Fixed, or Mephitic." The translations will be reproduced almost exactly as they left Crum Brown's hands, only a few minor slips and inconsistencies having been adjusted.

Black was a distinguished pupil of William Cullen, who himself occupies a noteworthy position as a pioneer in Britain in insisting on the importance and value of a knowledge of chemistry and in delivering, first in Glasgow and afterwards in Edinburgh, courses of lectures on the subject and on its history to his medical students. Availing himself of the opportunity afforded by the enlightened attitude of Cullen towards his pupils in encouraging them to engage in making chemical experiments on their own account, and with the definite object of endeavouring to find an appropriate solvent for the calculus—a matter that was seriously exercising the minds of physicians at the time—Black carried out a well-considered and systematic series of experiments on Magnesia Alba. The details of these experiments are described in his thesis, but Black did not there give more than an indistinct foreshadowing of the important conclusions with respect to mild and caustic alkalies, subsequently deduced from them and from some additional experiments, that he set forth in his extended paper of June, 1755, which was printed in the "Essays and Observations, Physical and Literary, Read before a Society in Edinburgh and Published by Them" [Vol. 2, 157–225 (1756)].

While Black thought that some of his experiments were, as he puts it in the second portion of his dissertation, "worthy enough of record" and that an account of them "would not be unpleasing" to those of his fellow-students who were fond of chemical philosophy, he admitted that what he had written on magnesia alba "did not seem to have such a relation to medicine as the motive of the work required" and he therefore "decided to preface it with some notes. . .on the acid humour arising from food, for which alone magnesia serves as a remedy." These notes were omitted from the subsequent extended paper. That, at the outset at any rate, Black did not entertain any exaggerated ideas as to the importance of his experimental work is evidenced by the following passage contained in a letter concerning his thesis which he wrote to Cullen from Edinburgh under date 18th. June 1754:—"What do you think of printing the experimental work in the Physical Essays here? If the experiments are worth anything they will be stolen by others; but yet I would rather have it so than make them public, unless you think it would be of some sort of service to me" [Thomson's "Life of Cullen," Vol. 1, 51 (1832)].

+ + + + + +

ON THE ACID HUMOUR ARISING FROM FOOD

(CRUM BROWN'S TRANSLATION)

AS I WAS thinking of this, my first little inaugural work, Magnesia Alba spontaneously presented itself, and the subject pleased me, chiefly because its simplicity makes it more easily adaptable to the prescribed limits, and more suited to my powers. But when I considered what I had written on it, it did not seem to have such a relation to Medicine as the motive of the work required, and I accordingly decided to preface it with some notes, as short as possible, on the acid humour arising from food, for which alone magnesia serves as a remedy.

The food mostly used by man is derived partly from animals, but chiefly from vegetables.

But the nature of almost all vegetable matters is such that, when macerated in water, or dissolved in it, and kept at the temperature of the human body, they spontaneously fall into a certain internal motion, commonly called fermentation, at the same time emit a great quantity of air, and at last are converted, wholly or in part, into an acid humour; and this change is accelerated by the addition of vegetable substances already undergoing fermentation.

Almost all the vegetables we eat are liable to corruption of this kind; and indeed it will not be out of place to review them here in the order of their readiness to undergo it, putting first those which most rapidly become acid, and letting the rest follow according to their disposition to this change. But as I do not know of any observations or experiments hitherto made, which could give such an order absolutely, a short summary only of the observations bearing on the matter need be given; but, before doing this it is to be noted that the vegetable products ordinarily used for food may be divided into four classes: of which the first includes leaves and roots: the second fruits distinguished for sweet and saccharine juice, the product of nature or of art, as also their juice converted by fermentation into a vinous liquor: the third farinaceous seeds and the meal prepared from them in various ways: the fourth milk, which chiefly is formed from vegetables elaborated into a food most agreeable to nature. As far indeed as experience has taught, leaves and roots taken into the stomach more frequently become acid. Of fruits and their fermented juices those are more liable to this corruption which contain a larger amount of water: indeed the fruits themselves ferment more quickly than even the vinous liquors. Of things made of meal, those most frequently ferment in the stomach, in which the particles of meal are least ground down and kneaded. Milk again seems to be of those most rapidly taken into the blood, and so more rarely becomes acid in the intestines.

All these things when they have once become acid are not only unsuitable for the proper nourishment of

the body, but are altogether hurtful to it, as sufficiently appears from the cases of those who have often and copiously drunk vinegar.

Therefore the Creator has given man various organs, which no doubt have great and various uses, but seem chiefly to take care that this change, so injurious, does not occur to food taken into the body. Thus the stomach receives the food already acted upon by the saliva and smeared with much mucus from the fauces and œsophagus. In the stomach it is warmed at a mild and uniform temperature, protected from external air, agitated with a constant but gentle motion and compressed; it is gradually mixed with mucus and the copious liquid which exhales everywhere from the arteries; then brought down, by the successive contraction of the fibres of the stomach into the duodenum, where it gradually imbibes the bile and is diluted with the pancreatic juice; next it slowly descends into the small intestines and receives much liquid and mucus from them; then at last it is caught up by the lacteal and other absorbent veins, mixed with a great quantity of lymph brought back from nearly every part of the body, and quickly carried into the blood; that by intimate mixture with this fluid, and by very swift motion, it may itself be converted into blood.

These various liquids, properly mixed with food, are said in this way to hinder its fermentation: because, when they of themselves fall into corruption, it is of a putrid and alkaline kind, contrary as it seems to the acid, so that chyle made up of liquids so opposite to each other, cannot turn out to be of either kind; but retains its mild character for some time until it is carried into the stream of the blood. It seems to be also a special use of the cystic bile that by gently stimulating the intestines it gives them the due tension, and preserves their orderly motions.

But still the mixture of these liquids would not suffice to hinder absolutely the fermentation of the food, if it were allowed to stagnate long in the stomach and intestines. Therefore stagnation and delay are hindered by the perpetual agitation of the stomach and bowels, originated no doubt by the motion of the surrounding parts, and constantly renewed by the successive contraction of the fibers of the stomach itself and of the intestines, so that the food is continually mixed with the liquids, driven on, shaken, and forced to pass into the absorbent vessels; for that alternate and gentle pressure promotes its absorption is both agreeable to reason and is proved by the beautiful experiment of the distinguished Dr. Kaau, who made chyle itself and also water pass into the lacteal vessels from a portion of the small intestine of a dying or already dead dog by gently agitating it in imitation of peristaltic movements.*

If we consider the process of digestion it will be clearly seen that bodily motion and exercise promote it, and hinder the fermentation of the food, but that on the other hand, rest and quiet should retard it, and in a measure induce fermentation of the food: for bodily motion or exercise shakes the food, moves it on, increases its alternate compression and agitation, and so its absorption; also by increasing the velocity and force of the blood, it promotes the secretion of the various liquids which are of use in digestion. But inactivity and repose make the blood move more slowly: hence a smaller quantity of it flows through the glands, the liquids in them in a measure stagnate and thicken, every secretion, and so also that of the liquids that should be poured on the food, is diminished: the food moves more slowly along the alimentary passage and is less shaken; hence if there is delay and repose, there is less impediment to fermentation.

And as the difference between a strong and a weak body is nearly the same as that between an exercised and an indolent body; the forces opposing the fermentation of the food must, *ceteris paribus*, be stronger or weaker according to the vigour or debility of the whole body.

In some bodies the action of digestion is performed with such force that it subdues the vegetable food most prone to fermentation and quickly turns it into good blood, but in others the action is so weak and imperfect that it is incompetent to digest it, it then ferments in the stomach, becomes acid, and the disease of which we are treating is produced.

The weakness or defect of the actions by which digestion is performed may have as causes weakness of the whole body, want of motion and exercise, a disease of some viscera by which either the secretion of a liquid necessary for proper digestion is hindered or the propulsion and absorption of the chyle is retarded, or lastly affections of the mind which often disturb all natural actions. Debility of the whole body often arises from a great loss of wholesome juices, or sometimes from the suppression of some particular evacuation. Diseases of the viscera, which hinder the secretion of liquids or delay the progress of the chyle may be sometimes clammy mucus clogging the glands, schirrus, scrofula, and the like blockading the various organs of digestion.

The fermentation of the food is a source of many ills; for the air, of which there is a great quantity given off, in its wanderings through the intestines, produces borborygmi and flatus, and sometimes inflations and enormous pains, as the intestine, constricted on both sides, including the air, denies it a vent. And indeed it seems likely that that air will be in all respects like every other air arising from fermenting liquids, and be full of a vapour so noxious to life that it suddenly suffocates animals that have breathed it, and therefore the spasms of the fibres of the stomach and intestines with which patients are very often troubled may to some extent be produced by the action of this air on the nerves.

There is indeed much of this air in food, as it is at first taken into the body, deprived, it is true, of elasticity, nor does it ever recover elasticity in a strong healthy body, but is carried together with the food into the blood, also along with it a quantity of air, by no

* *Kaau perspiratio dicta Hippocrati*, parag. 483 *et seq.*

means insignificant, entangled among the food in the mouth, and thereafter deprived of its elasticity by the digestive forces. There is certainly air in blood and in all liquid secretions. A great quantity can be extracted from the solid parts by means of heat, so that it must also be in the nutrient liquid: hence it appears to be necessary for the proper composition of all these things.

It is not to be doubted indeed that this air, extensively united with every part of our body, serves many great uses; nor is it to be supposed that its absence could be borne without inconveniences: but we do not seem to know what its use is, or what are the inconveniences that would result from its absence. Perhaps some of the colour of the blood and the solidity of its globules may be due to it, and perhaps its presence may make the blood more fit to stimulate gently the nerves so that a certain alacrity and vigour may be imparted to the vital and to the natural actions.

Those who suffer from acid have always a weak pulse; and daily become more languid, inert, and weak; the solid parts of the body become flaccid, the blood becomes pale and as it were vapid; all these symptoms may perhaps be ascribed to some extent to a deficiency of air in the blood and humours.

The acid when formed, is often eructed into the mouth, where it annoys the wretched patients with its very offensive taste and smell. By irritating the very sensitive entrance of the stomach it causes pain, burning the pit of the stomach, and, from the sympathy of this with the head, also headache and redness of the face. Mixed with new food it then acts as a ferment, so that this goes to the same corruption. Hence good, well prepared chyle is scarcely to be looked for; hence the blood, its source being depraved, itself becomes worse; and in a measure the whole body becomes pale, enervated, and thin: the organs of digestion themselves at the same time are weakened, and the disease itself increases. Meanwhile the quantity of acid increases daily, becomes more pungent by stagnation, irritates the stomach, creates a feeling of pain and hunger, which yet is little relieved by taking food.

If the acidity attains a higher degree it eludes the apparently very efficacious digestive action of the bile, making the bile, already very inert, more inert still, giving it that green colour, which it acquires when joined with any other acid; thence brought into the intestines it stimulates them, causes diarrhœa, with green fæces smelling manifestly of the acid: and then, the disease daily increasing, the digestive powers are so diminished that food, scarcely changed, passes through the whole intestinal canal, and lientery at length so overwhelms the wretched patient that, as by starvation, he is wasted almost to a skeleton.

The diagnosis and prognosis are sufficiently shown by what has been said. The cure is to be set about.

I. By changing or absorbing the acid.

II. By purifying the organs of digestion, and depriving them of the impure products of fermentation.

III. By forbidding foods liable to become acid, and in their place giving such as are easily digested.

IV. By strengthening and assisting the organs of digestion, and removing everything that impedes their action.

The acid is changed by alkaline salts and absorbent powders: these indeed unite with the acid to form a *tertium quid*, yet quite diverse from them both.

The *primae viae* are to be cleansed by a mild emetic or cathartic, selected from the aromatic, stimulant, strengthening bitters. For this in the first place aloes and rhubarb present themselves.

Magnesia alba answers both purposes, if administered with a pleasing aromatic.

As to diet, those vegetables which are more prone to fermentation are to be avoided, and animal food chiefly used, as it neither has this fault nor is difficult of digestion: and indeed of animals, or parts of them, those are to be chosen which are either naturally most easily digested, or can be made so by art. Such food to be taken in small quantity but often.

The organs of digestion are to be strengthened and helped by gently astringent and stimulant remedies, chalybeates, bitters, aromatics, pure wine, inspissated ox gall. Bitters seem in the first place suitable for this business, for they powerfully inhibit fermentation, and, by a certain stimulus, not unlike the stimulus of the cystic bile, incite the action and the movements of the intestines.

If digestion takes place languidly on account solely of the weakness of the whole body, the body must be brought back to health in divers ways, as the general debility arises from divers causes: for if it proceeds from a great loss of wholesome juices, the body is to be succoured by again gradually restoring it by the use of easily digestible food, or also of gently strengthening medicaments, which promote digestion: if it has taken its rise from the suppression of particular evacuations, these are to be again restored.

When digestion is languidly performed on account of lack of motion and exercise, the treatment is obvious. If again this disorder arises from the disease of an organ which takes part in the formation of chyle, this is to be diagnosed and treated according to its nature.

If from affections of the mind; these are to be allayed and at the same time orderly emotions restored by stimulant, aromatic, rather fetid medicaments.

NEW MODELS OF OLD MOLECULES—*A Correction*

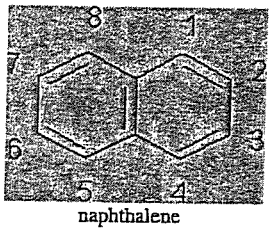
The illustration, Figure 2*e*, page 130 of Volume 12 of THIS JOURNAL (March, 1935) is marked "ethyl alcohol, acetone, and acetic acid." The label should read "ethyl alcohol, acetaldehyde, and acetic acid."

[Back to Study Aids]

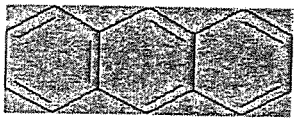
Nomenclature Needed for the Second Semester Course

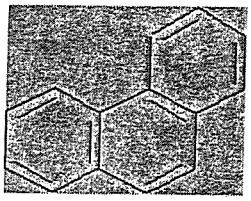
H. Nomenclature of Polycyclic Aromatic and Aromatic Heterocycles *Answers*

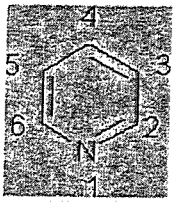
The following fundamental structures should be learned for the course. You should be able to name the base structure as well as simply substituted derivatives. If numbers are not given, you will not have to name substituted derivatives.



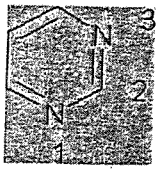
naphthalene


anthracene

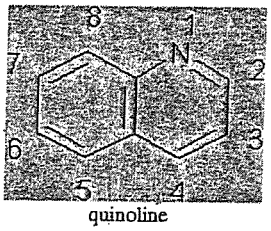

phenanthrene



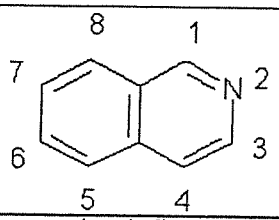
pyridine



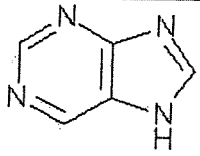
pyrimidine



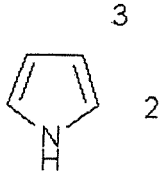
quinoline



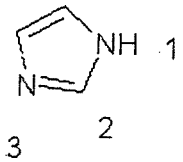
isoquinoline



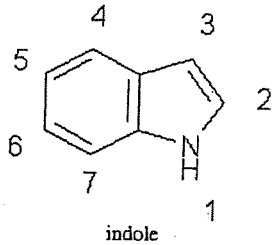
purine



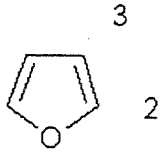
pyrrole



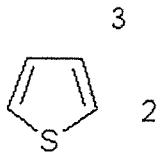
imidazole



indole

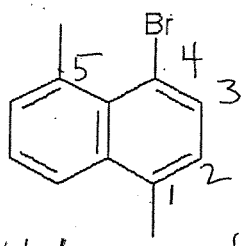


furan

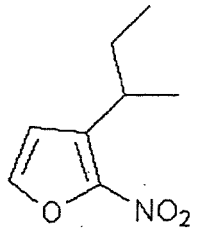


thiophene

Try to name the following substituted, aromatic heterocycles.....



4-bromo-1,5-dimethyl naphthalene

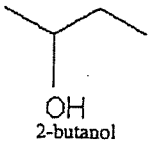


2-(1-methylpropyl)-2-nitro furan

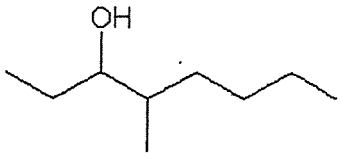
I. Nomenclature of Alcohols

Alcohols are named using the alkane root name, but the . e. is dropped and replaced with the alcohol ending . -ol. . A number is placed just ahead of the revised root name specifying the position of the -OH group. It is important to note that the alcohol functional group is considered to be higher priority thant the alkene or alkyne group. This means that when a molecule has multiple functional groups including hydroxyls, double bonds and triple bonds, you pick the longest continuous chain containing the alcohol or alcohol groups and you number the chain so that the alcohol groups have the lowest positions possible.

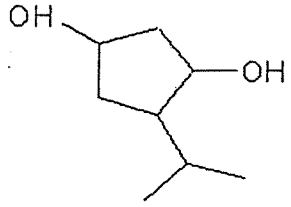
Consider the following examples.



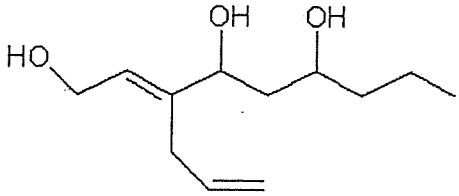
2-butanol



4-methyl-3-heptanol



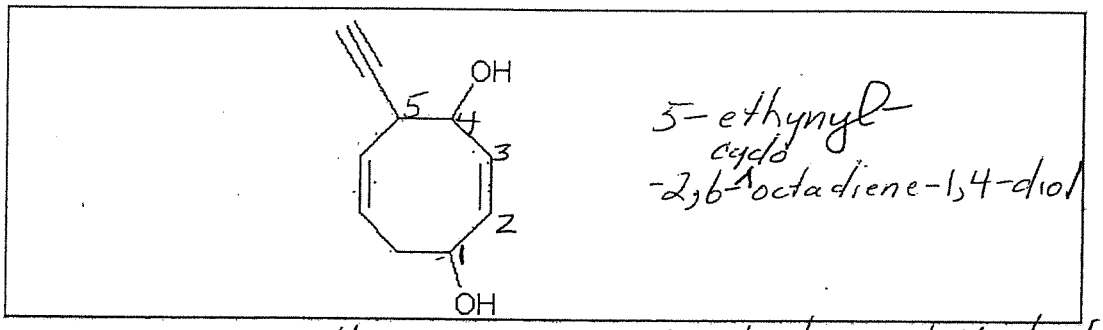
4-isopropyl-1,3-cyclopentanediol



3-(2-propenyl)-2-nonene-1,4,6-triol

Notice in the third example that the numbering in the ring must start at an alcohol position and pay particular attention to the nomenclature in the last example. The side chain is a complex side chain and since the main chain has two different types of functional groups both are incorporated into the root name as shown. The number for the alkene functional group in the main chain appears just before the root name while the numbers for the hydroxyl groups appear just before the alcohol suffix.

Try to name the following compound.



5-ethynyl-cyclo-2,6-octadiene-1,4-diol

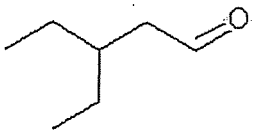
5-ethynyl-2,6-cyclooctadiene-1,4-diol

J. Nomenclature of Aldehydes and Ketones

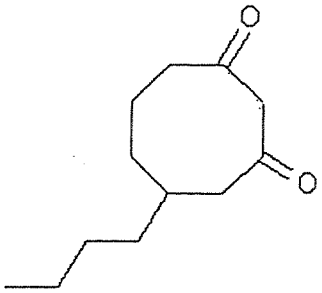
Simple aldehydes and ketones are named similarly to alcohols. The fundamental alkane names are used, but the . e. is dropped and replaced with . al. and . one. , depending on the situation. In terms of priority, both groups are higher than alcohols, but between the two, the aldehyde is highest. This means that if the aldehyde and ketone appeared in the same molecule, you would give chain and numbering preference to the aldehyde.

You will note that the aldehyde group is always a terminal group so in most structures numbering is redundant and can be left out.

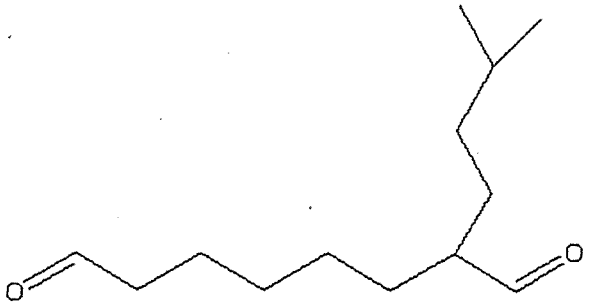
Please study the following examples.



3-ethylpentanal



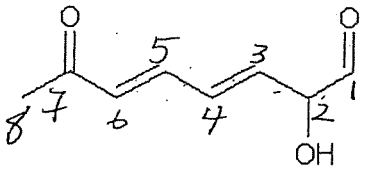
5-butyl-1,3-cyclooctanedione



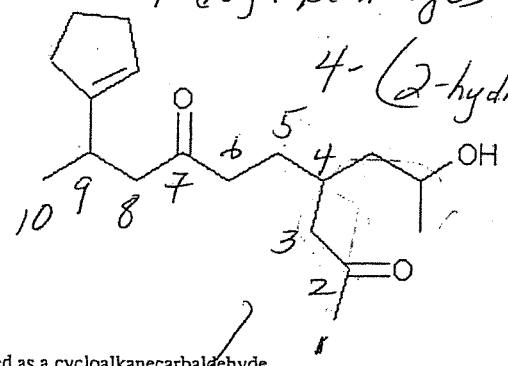
2-(3-methylbutyl)-octanedial

Try to name the following structures

2-hydroxy-7-oxo-3,5-octadienal

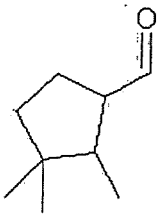


9-(cyclopentenyl)-4-(2-hydroxypropyl)



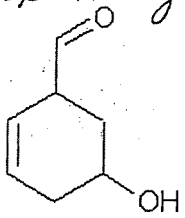
Sometimes an aldehyde appears on a ring. Given its high prority the ring is named as a cycloalkanecarbaldehyde.

Please consider the following examples.



2,3,3-trimethyl-cyclpentanecarbaldehyde

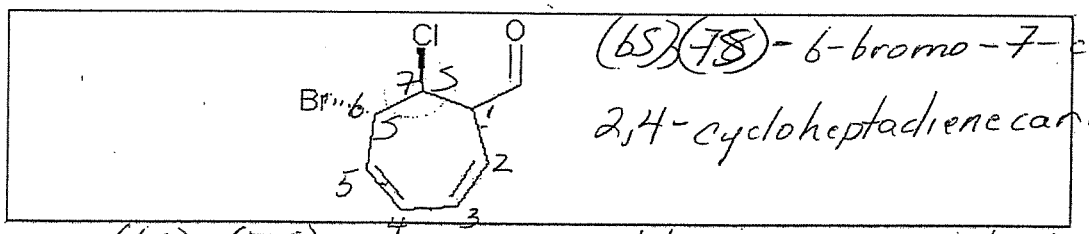
9-(1-cyclopentenyl)-4-(2-hydroxypropyl)-2,7-decanedione



3-hydroxy-5-cyclohexenecarbaldehyde

Notice in the second example that the alcohol group is called a hydroxy because it is lower priority than the aldehyde. Also please note that the alkene is given last consideration in terms of numbering.

Please attempt to name the following compound.

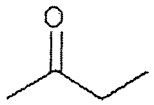


(6S)(7R)-6-bromo-7-chloro-2,4-cycloheptadienecarbaldehyde

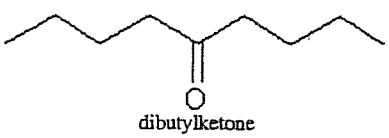
(6S),(7S)-6-bromo-7-chloro-2,4-cycloheptadiene-carbaldehyde

As a review try to designate the absolute stereochemistry of the stereocenters.

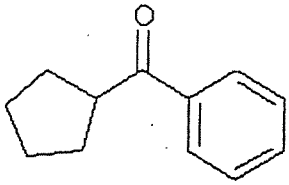
Ketones are frequently named using their common names which involves simply giving alkyl-type names to the two chains coming off the ketone and following those names with the word . ketone. . The following examples illustrate this trivial, but accpetable nomenclature.



ethylmethylketone



dibutylketone

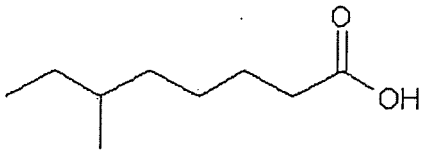


cyclopentylphenylketone

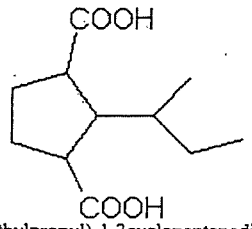
Please note that the two substituents are ordered alphabetically in the common name. In alphabetizing, the prefixes: t-, sec-, di-, tri-, etc. are ignored. The prefixes neo-, iso-, cyclo- are considered. In complex side chain names (the ones in parenthesis) , the first letter encountered is used in the ordering.

K. Nomenclature of Carboxylic Acids

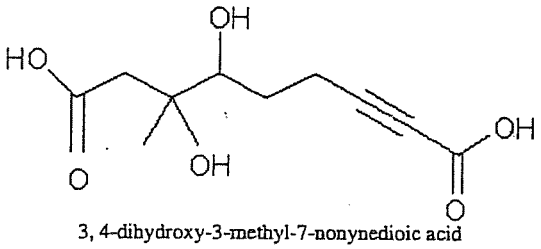
Carboxylic Acids have a lot in common with aldehydes since they are terminal groups and by structural necessity must be peripheral on rings. The one difference to note is that they are higher priority than aldehydes. At this point, I figure you can get the drift of carboxylic acid nomenclature by just absorbing a few good examples.....



6-methyl-octanoic acid

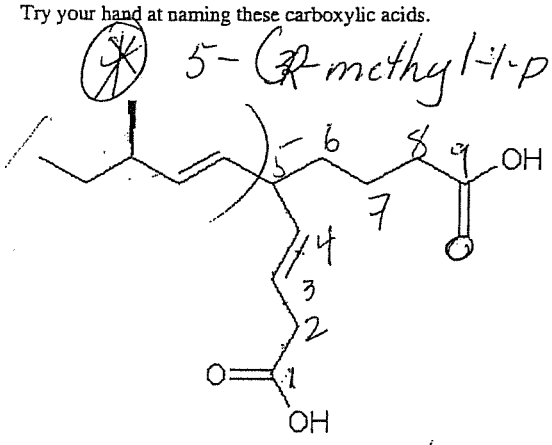


2-(1-methylpropyl)-1,3cyclopentanedicarboxylic acid



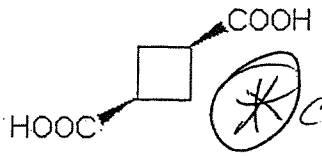
3, 4-dihydroxy-3-methyl-7-nonynedioic acid

Try your hand at naming these carboxylic acids.



5-(2-methyl-1-pentenyl)-3-nonenedioic acid

3-nonenedioic acid



cis-cyclobutane dicarboxylic acid

Please include the absolute configuration of any stereocenters.

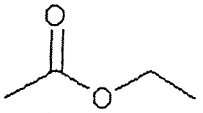
L. Nomenclature of Carboxylic Acid Derivatives

You will not be expected to be supreme experts on these derivatives, but you do need to know the basics of naming them. The esters are the most important so these will be covered the most rigorously.

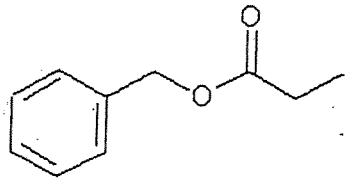
Esters

Esters are named the way salts are named. Think about the sodium salt of acetic acid. It is called sodium acetate. For an ester, the sodium would be replaced by the appropriate alkyl name for the substituent on the oxygen of the ester functional group.

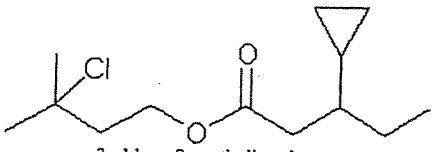
Please consider the following examples....



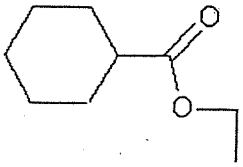
ethyl acetate (less commonly called ethyl ethanoate)



benzyl propionate

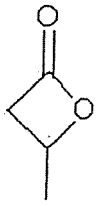


3-chloro-3-methylbutyl 3-cyclopropylpentanoate



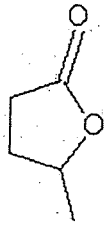
ethyl cyclohexanecarboxylate

Cyclic esters are called lactones. A few examples are given below. You will not be responsible for the specific nomenclature of this subclass.



beta-butyrolactone

gamma-butyrolactone

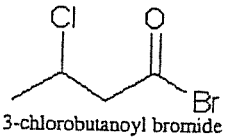


gamma-valerolactone

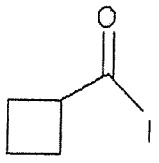
Acid (Acyl Halides)

Acid halides are named taking the . ic. ending off the corresponding carboxylic acid name and replacing it with . yl. and then adding the appropriate halide ending.

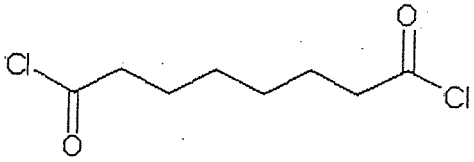
A few simple examples.....



3-chlorobutanoyl bromide



cyclobutanecarbonyl iodide

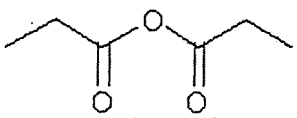


octanedioyl dichloride

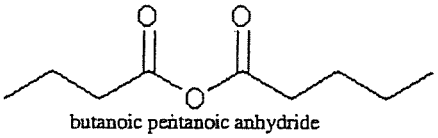
.nhydrides

Anhydrides are named in a manner similar to the trivial method for ketones. The two parent acids are given names and that is followed by the word anhydride.

Here are a few examples...



propanoic anhydride

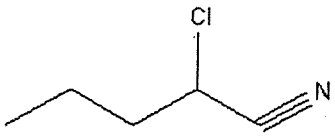


butanoic pentanoic anhydride

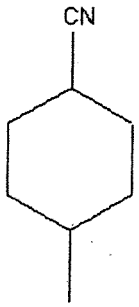
Notice that the two acid names are alphabetized when they are different and that when the anhydride is symmetrical, no di- prefix is used.

Nitriles and Amides

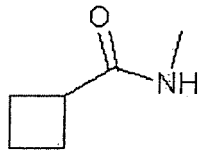
Please study the following examples.....



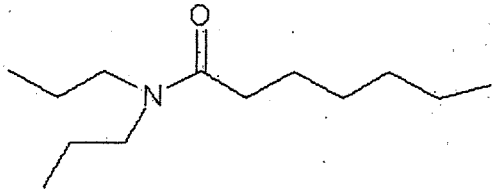
2-chloropentanenitrile



4-methylcyclohexanecarbonitrile

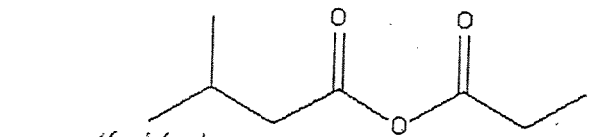


N-methylcyclobutanecarboxamide



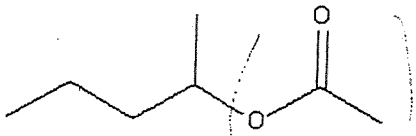
N, N-dipropylheptanamide

Try to name these carboxylic acid derivatives



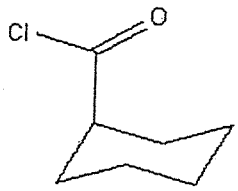
3-methylbutanoic propanoic

3-methylbutanoic propanoic anhyd

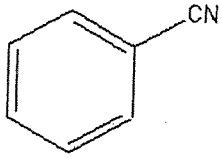


(1-methylbutyl) ethanoate

acetate

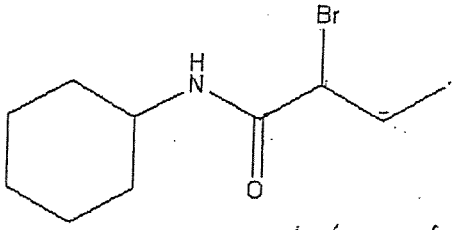


cyclohexane-carbonyl chloride



benzonitrile

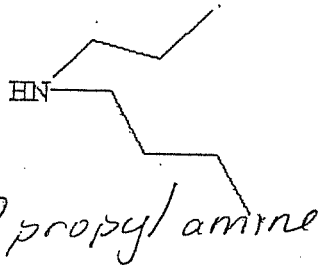
cyanobenzene



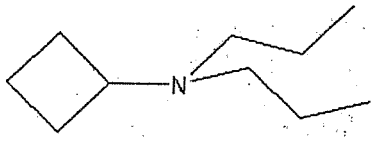
N-cyclohexyl-2-bromobutanamide

M. Amines

Amines are named like ethers. You give the chains attached to the nitrogen the normal alkyl names and follow them by . amine. . You should alphabetize the alkyl names and use multiple prefixes as needed. Try to name the following compounds.



butyl propyl amine



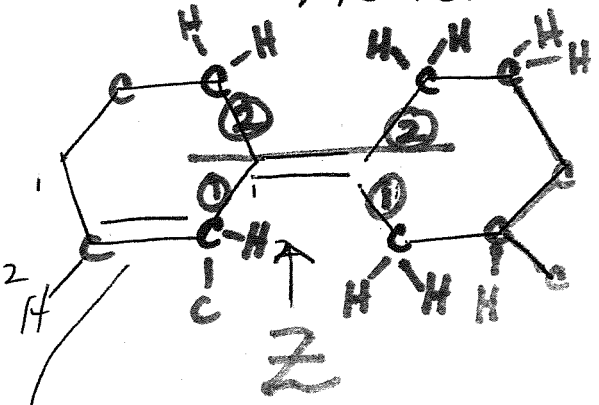
cyclobutyl dipropyl amine

[Back to Study Aids]

More in class Problem Solutions

9/28/02

ASSIGN Z/E

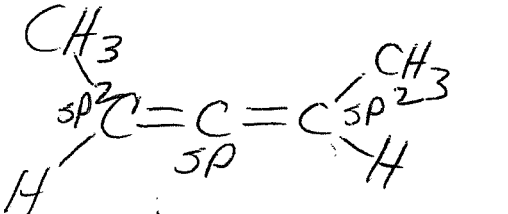


Z

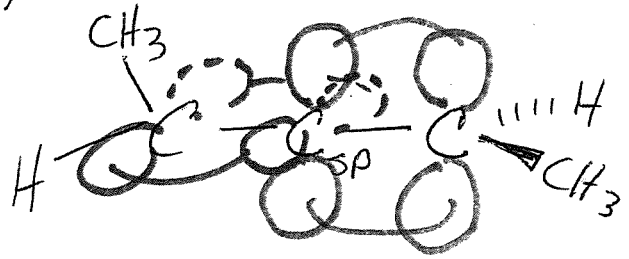
also Z, however, would be assumed to be Z because of constraints imposed by ring

9/28/02

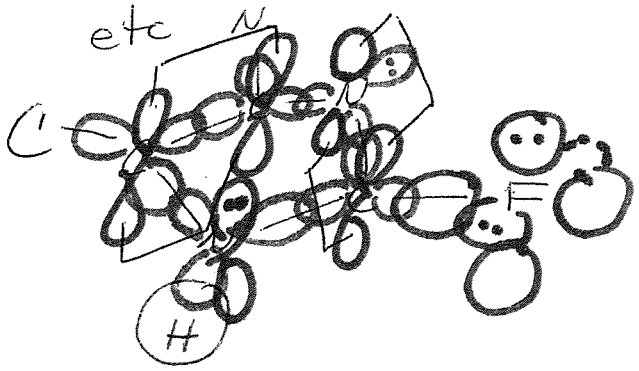
is this chiral?



→ in 3D this molecule looks like following



Orbital Diagram



Key: — ≡ p orbital

— ≡ S orbital

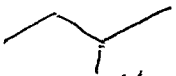
— ≡ sp^2 orbital

Physical Properties of Stereoisomers

* Enantiomers have the same physical properties

Have same b.p, m.p., solubility, spectra

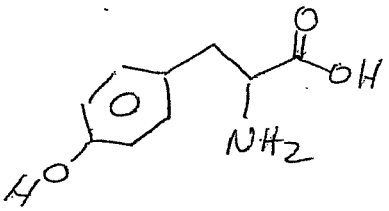
But Enantiomers Rotate Plane Polarized Light in Equal and Opposite Directions

e.g. R-2-butanol $-13.52 = [\alpha]^{D}_{25}$ 

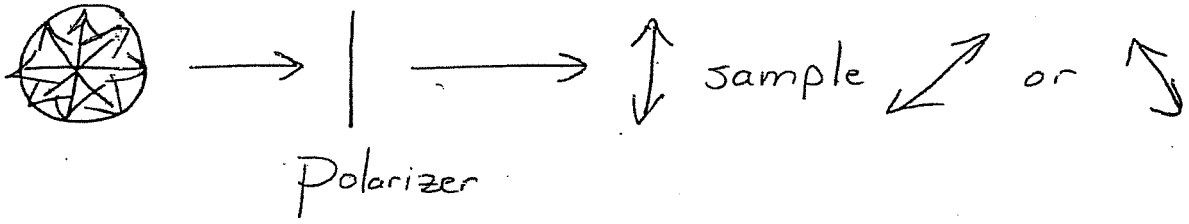
S-2-butanol $+13.52 = [\alpha]^{D}_{25}$

S-tyrosine −10.9

R-tyrosine +10.9



* Polarimetry (Show Real Polarimeter)



Plane polarized light is chiral

Though INDIVIDUAL correlations are made and individually correlated molecules can be identified by their specific rotations

THERE IS NO GENERAL CORRELATION BETWEEN SIGN OF ROTATION AND ABSOLUTE CONFIGURATION

(K) While nature is very successful at making one enantiomer, for a long time MAN was unsuccessful - Most syntheses resulted in 50:50 mixtures = racemates
racemic modifications
racemic mixture

Why is this a problem

What is rotation of a 50:50 mixture of enantiomers?

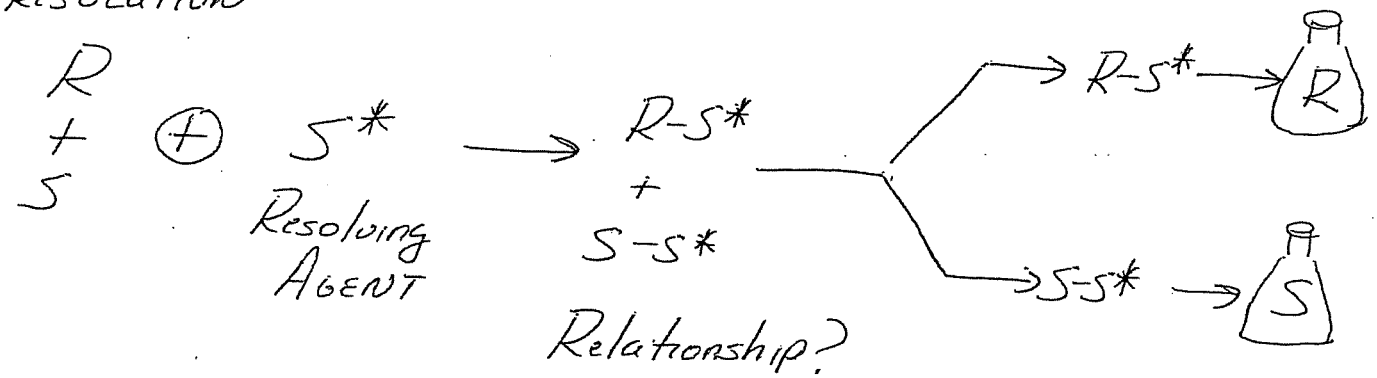
What is the rotation of a ~~50:50~~ Meso cmpd? Geneeal Achiral cmpd?

* Diastereomers: Different Physical Properties

Many cmpds in diastereomeric pairs have rotations (are chiral) but no relationship between rotations

⊛ Resolution vs. Chiral Synthesis

Resolution

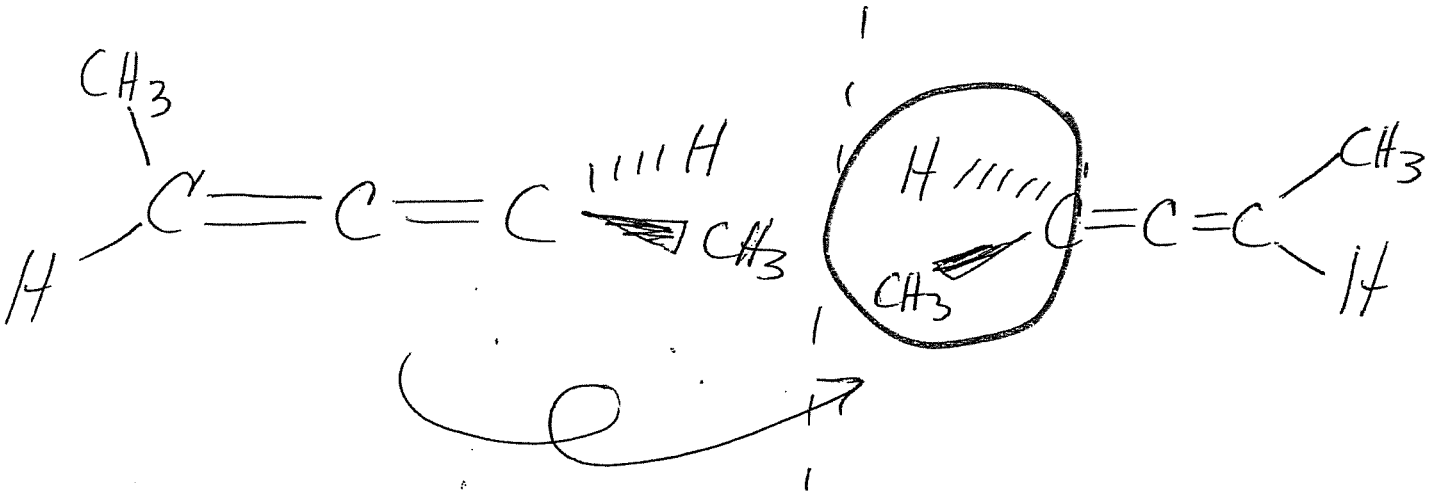


Chiral Synthesis

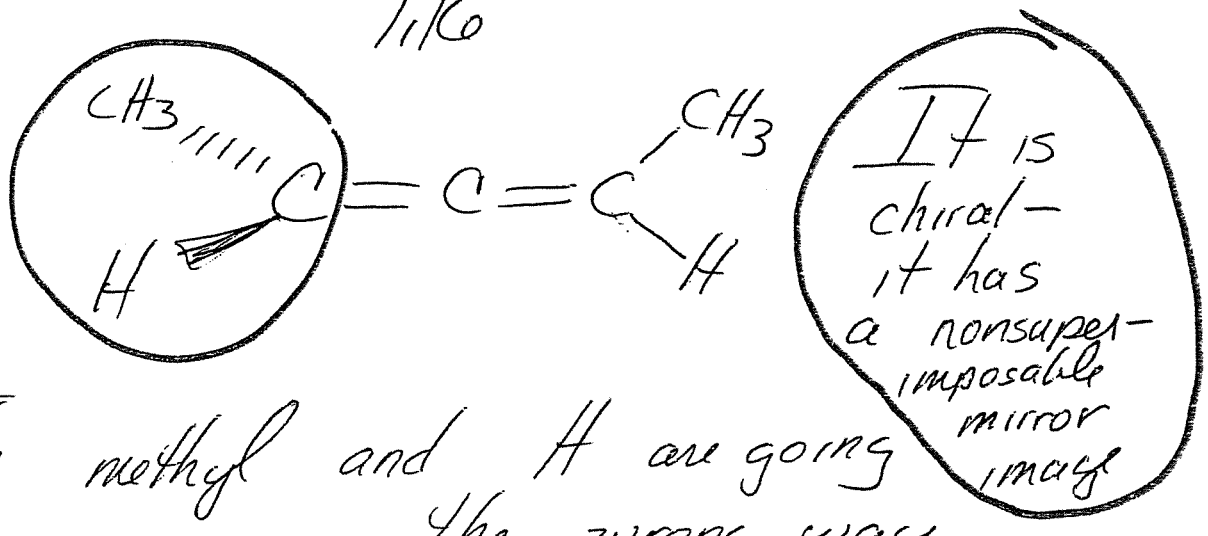
$$S^*\text{-}[Sub] + A \longrightarrow S^*\text{-}[Sub]'\text{-}A' \longrightarrow [Sub]'\text{-}A'$$

Is this Chiral.

The best way to test chirality is to draw the mirror image & test superimposability, i.e.,

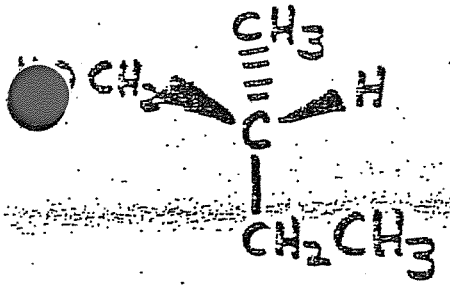


When you pick the first molecule up & turn it over to superimpose, it looks like



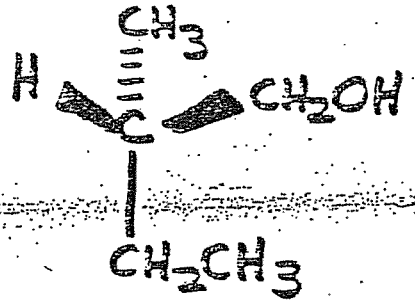
The methyl and H are going the wrong way

5.9.



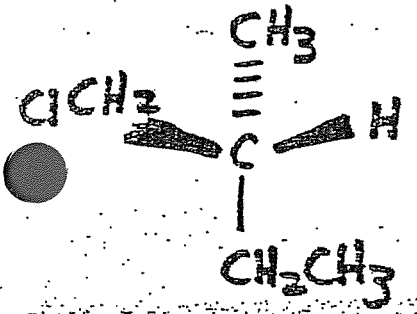
(R)-(+)-2-methyl-1-butanol

$[\alpha]_D^{25} = +5.756°$



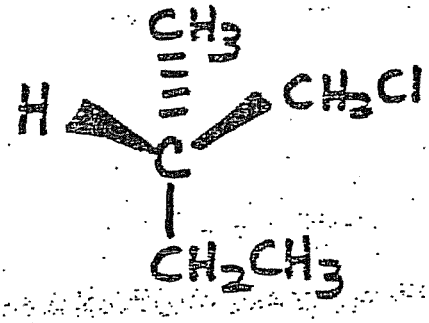
(S)-(-)-2-methyl-1-butanol

$[\alpha]_D^{25} = -5.756°$



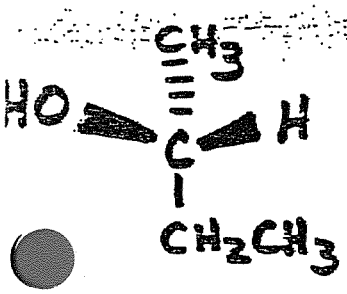
(R)-(-)-1-chloro-2-methyl butane

$[\alpha]_D^{25} = -1.64°$

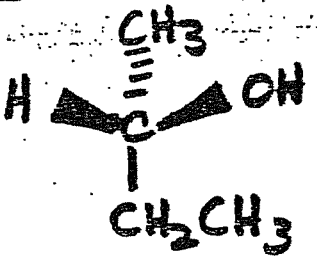


(S)-(+)-1-chloro-2-methyl butane

$[\alpha]_D^{25} = +1.64°$



(R)-(-)-2-butanol



(S)-(+)-2-butanol

Calculations:

$$\% \text{ yield} = \frac{\text{g resolved amine}}{\text{group amine g total}} \times 100$$

max = 50%

Alternatively divide by ½ group g of amine

max = 100%

$$\text{experimental } [\alpha]^D = \frac{\text{observed } \alpha}{c \cdot l}$$

we will see this today
function of Cmpd
? # of molecules
Pnt in path of light
Bigger sample - Bigger rotation

c = concentration g/mL

w/ Limonene be sure use density on bottom for wks. 4

l = cell length dm

$$\% \text{ optical purity} = \frac{[\alpha]^D \text{ exp}}{[\alpha]^D \text{ lit.}} \times 100$$

Enantiomers D-2

What does the optical purity mean?

50% excess S

50% racemate

S S R R

S S S S

RATIO

R : S

25 : 75

Click the page number to move to the next page.
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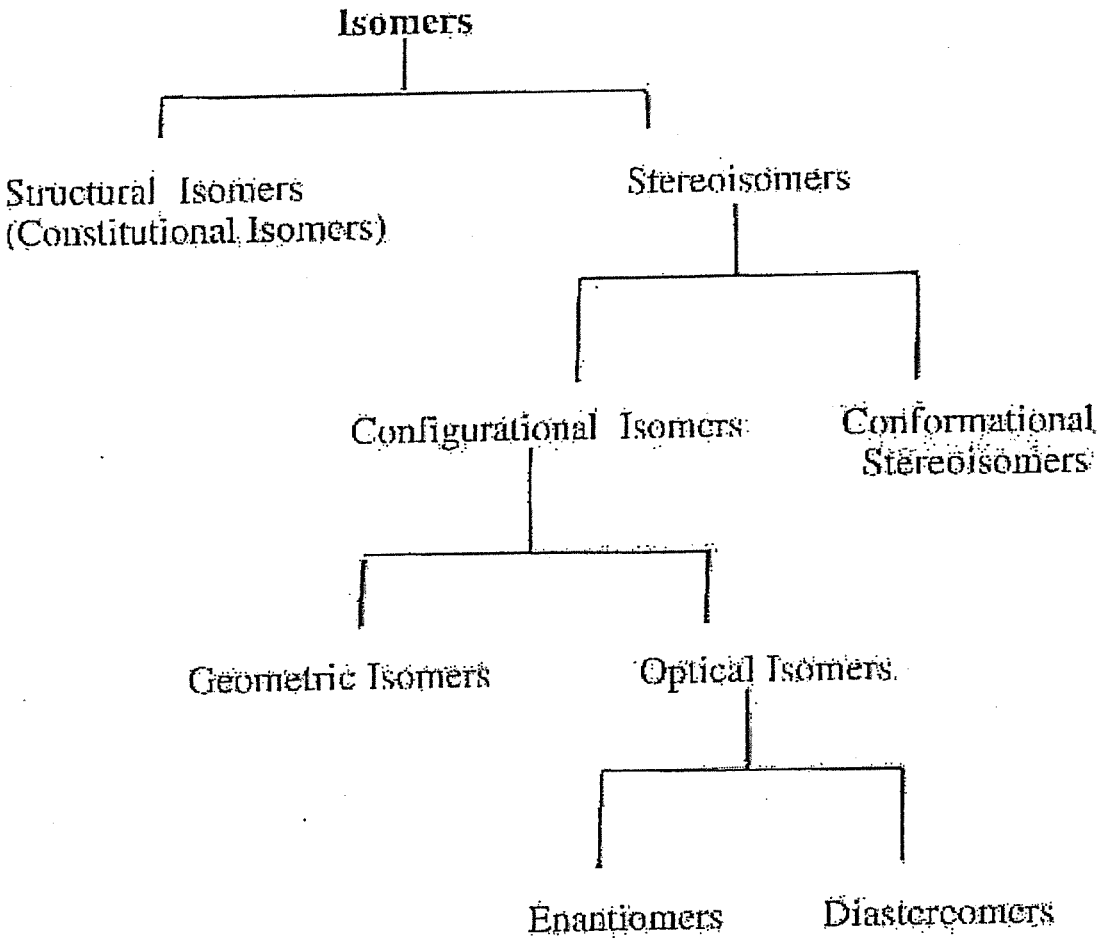
Overview of Isomerism Including Stereoisomerism



Some Definitions

Structural Isomers: (includes position isomers) Compounds that have the same formula, but different connectivity. These compounds have different IUPAC names.

Stereoisomers: Compounds that have the same formula, same connectivity, but groups are oriented differently in space.

Conformational stereoisomers: Stereoisomers that result from the rotation of a sigma bond. Conformers can be interconverted at room temperature and cannot be separated and placed in different bottles. They exactly the same IUPAC name and Cahn-Ingold-Prelog designation.

Click the page number to move to the next page.
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Configurational Isomers: Stereoisomers that can only be interconverted by breaking sigma or pi bonds. These have the same IUPAC name, but different Cahn-Ingold-Prelog designations.

Geometric Isomers: The so called cis/trans isomers involving double bonds or rings.

Optical Isomers: Compounds that have a stereochemical relationship, but also rotate plane polarized light when pure.

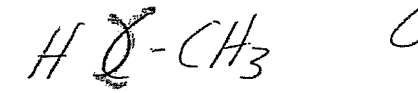
Enantiomers: Stereoisomers that are nonsuperimposable mirror images.

Diastereomers: Stereoisomers that are nonsuperimposable and not mirror images. Please note that geometric isomers are technically diastereomers even though they do not necessarily rotate plane polarized light.

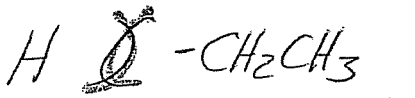
Conformational Analysis

Some solved problems

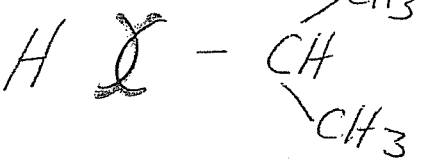
① Explain the following energies for 1,3-diaxial interactions (steric interaction)



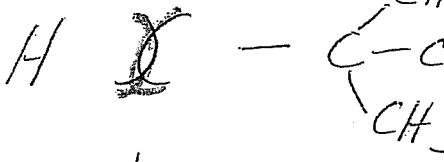
0.90 kcal/mol



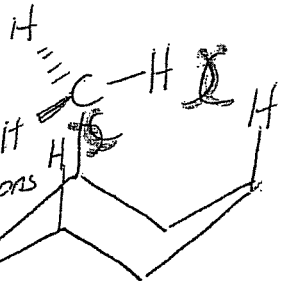
0.95 kcal/mol



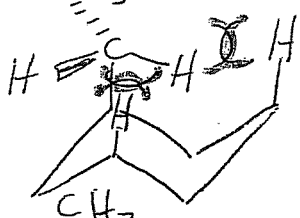
1.1 kcal/mol



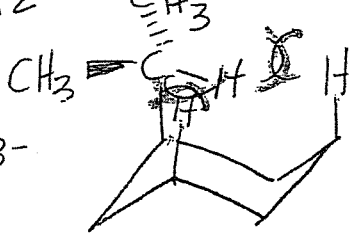
2.7 kcal/mol



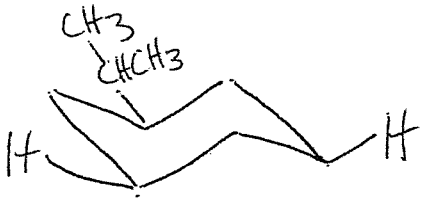
2 1,3-diaxial interactions
0.90 X 2
= 1.8 kcal

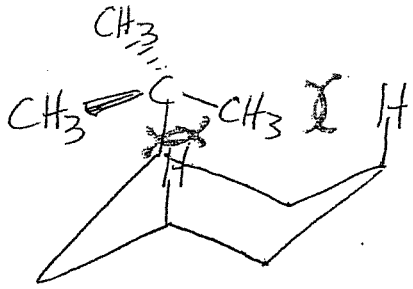


2 1,3-diaxial interactions
0.95 X 2
= 1.90

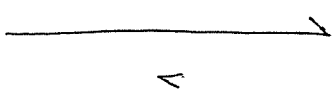


2 1,3-diaxial interactions
1.1 X 2
= 2.7





? 1,3 diaxial nteractions



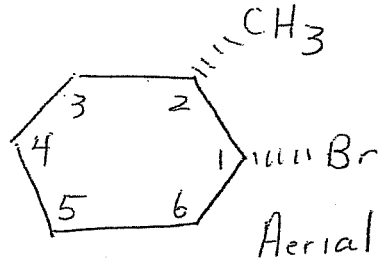
~ 99.9%

?.7 X2 = 5.4 kcal/mol

The reason the energies stay about the same for methyl, ethyl and isopropyl is that these groups can all orient in such a way that a hydrogen (rather than a methyl) is facing in toward the interior of the ring (pointing toward the ~~een~~ axial hydrogens). The tertiary-butyl group can't do this - a methyl must point toward the axial hydrogen - raising the steric interaction considerably.

Please note that the t-butyl group is so large that the equatorial conformer represents almost 100% chairs.

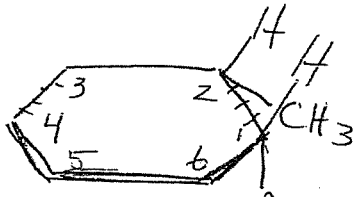
(2) Carry out a conformational analysis of 1R,2S-1-bromo-2-methylcyclohexane



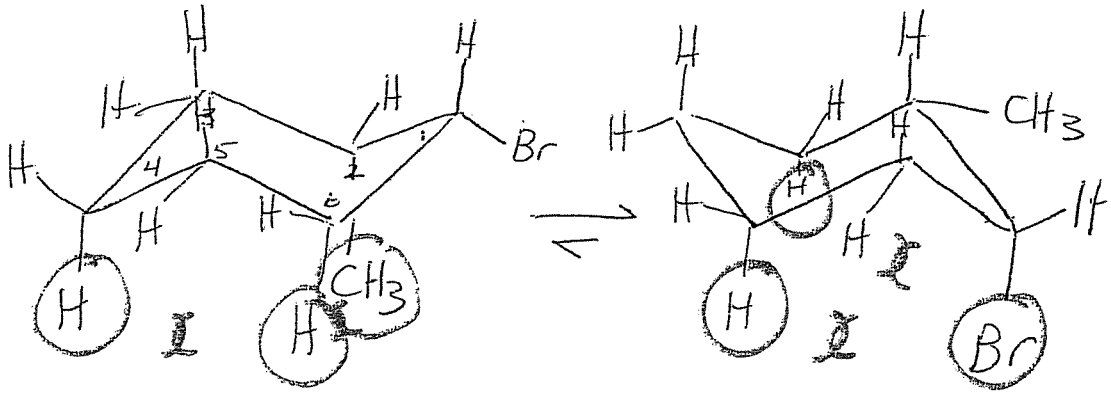
Aerial

Note this is a "cis" cmpd

≡



Side View



2 1,3 diaxial ints

2 1,3 diaxial ints

each $-CH_3$ ⊄ H costs 0.9 kcal/mol

$2 \times 0.9 = 1.8$

each −Br ⊄ H costs 0.25 kcal/mol

$2 \times 0.25 = 0.50$

This is lower energy conformer

Drawing Resonance Forms Systematically

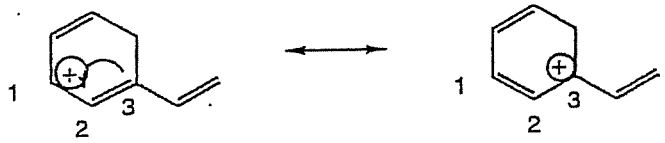
1. CHARGED SPECIES AND RADICALS

When dealing with a charged species or radical the goal is to show the distribution of the charge/radical through the π system **step by step**. This can be done systematically using the arrow formalism, e.g.,

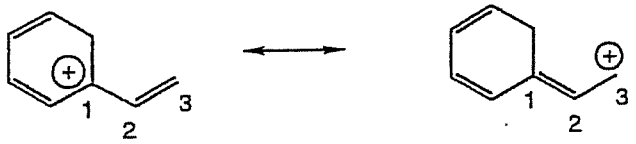
CARBOCATIONS

To generate the structures, it works to view the electrons adjacent to the charged atom as though they are a fence on a hinge. Swing the "fence" from between 2 & 3 over to 1 & 2. Leave all other bonds the same.

Now the charge is near a new double bond. Carry out the same operation.



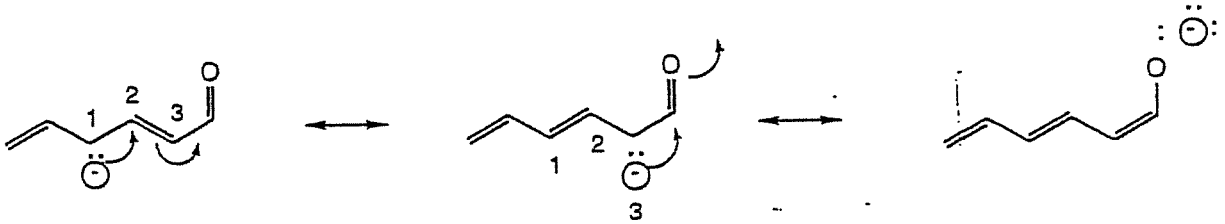
Once again ....



CARBANIONS

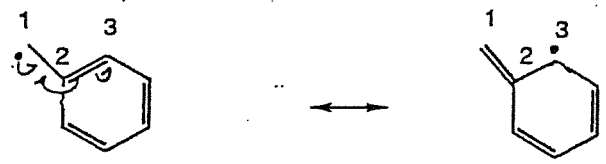
For carbanions, the flow of electrons is in the opposite direction. Take the pair of electrons and push them between 1 and 2. This will leave too many electrons around 2, so swing the electrons between 2 and 3 out onto 3.

Continue this process, step by step.

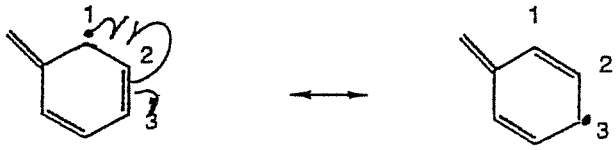


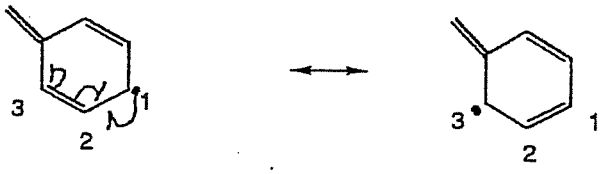
RADICALS

For radicals, the unpaired electron at 1 and one of the π electrons between 2 and 3 are combined to form a π bond between 1 and 2 leaving an unpaired electron at 3.



Continuing ...



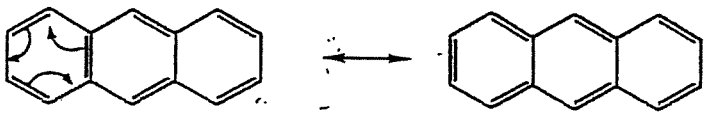


2. NEUTRAL AROMATIC SPECIES INCLUDING FUSED, POLYCYCLIC AROMATICS

When dealing with neutral molecules such as fused, polycyclic aromatics one often has to completely circulate the electrons around a ring to generate another important structure(s). For example, consider the resonance forms of benzene. This is because step by step circulation as done earlier in this handout will generate new charge.

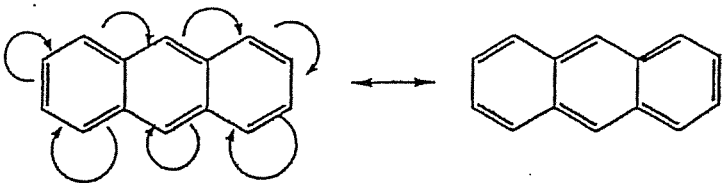
The following are some guidelines using anthracene as an example.

a. Circulate electrons around any existing benzene rings, the goal being to get alternating d.b.'s around the outer ring. Shown below.



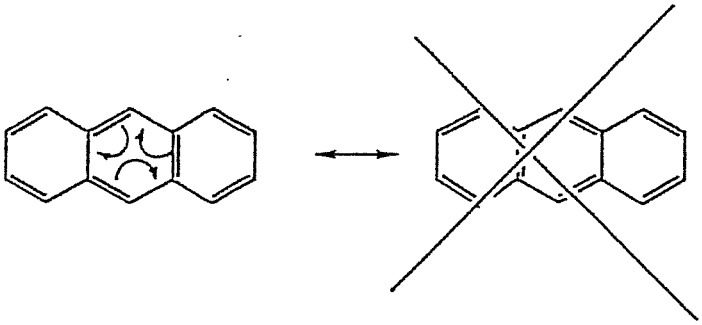
Anthracene

b. Having acomplished the goal, circulate the electrons completely around the "outer" ring. Shown below.



c. Now circulate electrons around any "new" benzene rings you have generated as shown below.

d. Repeat the process as in (c) until you start to regenerate previously drawn structures. If regeneration occurs you are normally finished.

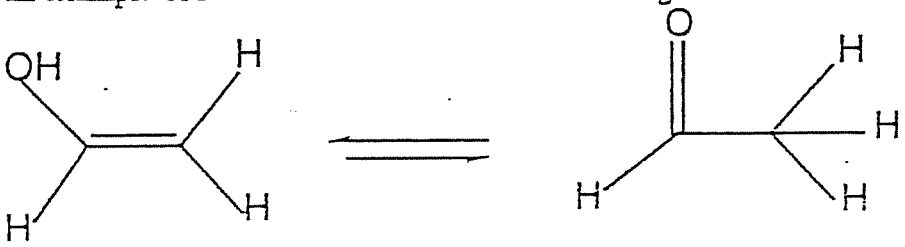


(redundant
same as original)

Rules for Writing Resonance Structures

1. Resonance Structures exist only on paper. No individual structure represents the entire structure. The structure is a weighted average or hybrid of the individual structures.

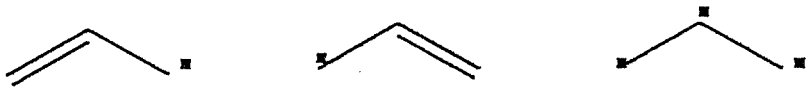
2. In generating resonance structures, one can only move electrons. The following is not an example of resonance because atoms are moving.



keto-enol tautomerization

3. As much as is possible, resonance structures should be proper Lewis structures, i.e., obey octet rule, correct no. of bonds, etc.

4. All the resonance structures must have the same number of unpaired electrons, e.g.,



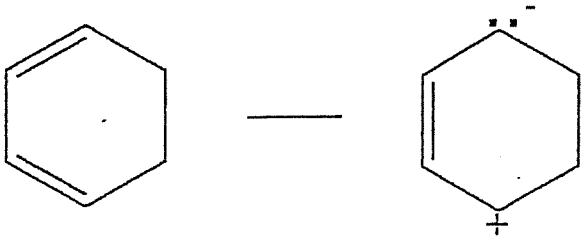
5. All of the atoms that are part of the delocalized system must lie in a plane or be nearly planar.

Rules Concerning the Energy of Hybrids and Contributing Forms

1. The energy of the actual molecule is lower than the energy of any contributing structure. This is what is meant by the term resonance stabilization.

2. Equivalent structures make equal contributions to the hybrid. Systems having equally contributing structures have a large stabilization.

3. The more stable a structure is alone, the greater its contribution to the hybrid. Factors that can be used to evaluate the importance of a given resonance form are the number of covalent bonds (more are better), the number of electrons in the valence shell when bonded (eight is best) and charge separation (less is better). The following examples illustrate these points.



Most Important

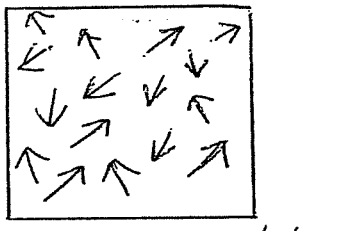
Most Important

Most Important

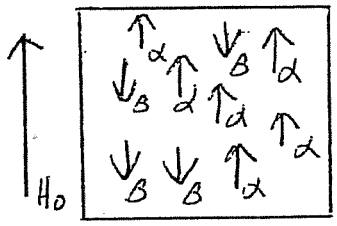
The Basics Nuclear Magnetic Resonance Spectroscopy

Nuclei possessing angular moment (also called spin) have an associated magnetic moment. A few examples of magnetic isotopes are ^{13}C, ^{1}H, ^{19}F, ^{14}N, ^{17}O, ^{31}P, and ^{33}S. Please note that not every isotope is magnetic. In particular you should note that ^{12}C is not magnetic. If a nucleus is not magnetic it can't be studied by nuclear magnetic resonance spectroscopy. For the purposes of this course, we will be most interested in ^{1}H and ^{13}C. I will limit my discussions to ^{1}H in this short treatment. Generally speaking, you should think of these special nuclei as tiny, atomic, bar magnets.

Nuclear Magnetic Spectroscopy is based on the fact that when a population of magnetic nuclei is placed in an external magnetic field, the nuclei become aligned in a predictable and finite number of orientations. For ^{1}H there are two orientations. In one orientation the protons are aligned with the external magnetic field (north pole of the nucleus aligned with the south pole of the magnet and south pole of the nucleus with the north pole of the magnet) and in the other where the nucleus is aligned against the field (north with north, south with south). The alignment with the field is also called the "alpha" orientation and the alignment against the field is called the "beta" orientation. From my description of the poles, which orientation do you think is the preferred or lower in energy? If you guessed the "alpha", you are correct. It might be worth noting at this point that before the nuclei are placed in the magnetic field they have random orientation.



random orientation outside field



α and β orientation in field

Since the alpha orientation is preferred, more of the population of nuclei are aligned with the field than against the field. You might wonder why any spins would align against the field. Realize that we are talking about **atomic** magnets. These are **very, very weak magnets**. The energy difference between the alpha and beta orientations is not large. There is enough energy for nuclei to exchange between the two orientations at room temperature, though a slight excess on average is in the lower energy, alpha state.

The nuclear magnetic resonance (NMR) spectroscopy experiment involves using energy in the form of electromagnetic radiation to pump the excess alpha oriented nuclei into the beta state. When the energy is removed the energized nuclei relax back to the alpha state. The fluctuation of the magnetic field associated with this relaxation process is called resonance and this resonance can be detected and converted into the peaks we see in an NMR spectrum.

What sort of electromagnetic radiation is appropriate for the low energy transition involved in NMR? Well believe it or not **radio waves** do the trick. Radio waves are at the very

low energy end of the electromagnetic spectrum and are sufficient to induce the desired transition. It is for this reason that NMR is considered to be a safe method of analysis. The same technology is now used in hospitals in MRI (Magnetic Resonance Imagining - people are afraid of the word nuclear). If you have ever had an MRI done, realize that you were placed in a magnetic field and all your magnetic nuclei lined up in the manner described above. Excess nuclei were pumped to higher energy states as you were exposed to radio waves.

The following are two very, very important points to accept and learn if you are going to understand the rest of the discussion.

1. **Electric currents have associated magnetic fields.**

2. **Magnetic fields can generate electric currents.**

If you haven't had physics yet, try to accept these two points. Certainly most people have at least heard of electromagnets and if so, you probably have some idea about the first statement.

The following is a very important NMR relationship. This expression relates the external field to the frequency of resonance.

$$\nu = \frac{\mu H_o}{2\pi}$$

In this equation, ν is frequency, μ is the magnetogyric ratio (not needed for this discussion - a constant for each nucleus) and H_o is the magnetic field. The big thing to glean from this equation is that the **external field and the frequency are directly proportional.** If the external field is larger , the frequency needed to induce the alpha to beta transition is larger. It follows then that in a larger field, higher frequency radio waves would be needed to induce the transition.

In this context it is relevant to note that different nuclear magnetic resonance spectrometers have different magnetic field strengths. For example the NMR on the first floor of Park Hall has a relatively high field, superconducting magnet. Because the field is high (high enough to erase bank cards and interfere with pacemakers and watches), the frequency range needed to excite protons is relatively high. It is called a 300 MHz (MHz = megahertz, a hertz is a cycle per second - a frequency unit) spectrometer, referring to the excitation frequency. The NMR on the second floor of park hall has a much weaker electromagnet associated with it. It is a 60 MHz instrument. Since different NMRs have different operating frequencies, spectra cannot be compared from different machines if they are reported in frequency units. For this reason, the universal PPM (parts per million) units are used in NMR. **Please note the following relationship between PPM and frequency. The fact that frequency and PPM are directly proportional is all you need to retain for the future discussion and the course in general.**

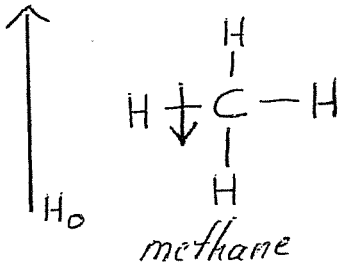
$$\textbf{chemical shift in ppm} = \frac{\textbf{peak position in Hz (relative to TMS)}}{\textbf{spectrometer frequency in MHz}}$$

Now let us use these basic ideas to better understand and interpret NMR spectra.

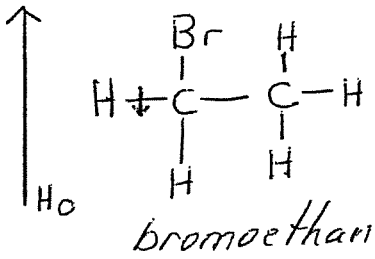
1. Why do we see peaks? When the excited nuclei in the beta orientation start to relax back down to the alpha orientation, a fluctuating magnetic field is created. This fluctuating field generates a current in a receiver coil that is around the sample. The current is electronically converted into a peak. It is the relaxation that actually gives the peak not the excitation.

2. Why do we see peaks at different positions? Realize that in principle, a peak will be observed for every magnetically distinct nucleus in a molecule. This happens because nuclei that are not in identical structural situations do not experience the external magnetic field to the same extent. The nuclei are **shielded** or **deshielded** due to small local fields generated by circulating sigma and/or pi electrons.

To understand this concept better, consider a "run of the mill" hydrogen like that in ethane or methane. When this sort of hydrogen is placed in a magnetic field, the sigma electrons start to circulate. **Remember : Magnetic fields generate currents.** When the electrons circulate, they generate a small magnetic field that happens to point in the opposite direction to the external field. **Remember: Currents have associated magnetic fields.** Since magnetism is a vector quantity (vector quantities have direction and magnitude), this local field reduces the overall field somewhat. Therefore, the described hydrogen experiences a reduced magnetic field. If we reconsider the important NMR equation given on page two of this document, we can only conclude that the external field is lower so the frequency of the electromagnetic radiation needed to induce the alpha to beta transition is lower. Remember that frequency and PPM are directly proportional. Therefore, if a hydrogen requires a lower frequency then it will show up as a peak at a lower PPM value. Hydrogens like those in methane are at around 1.0 PPM in the NMR spectrum.



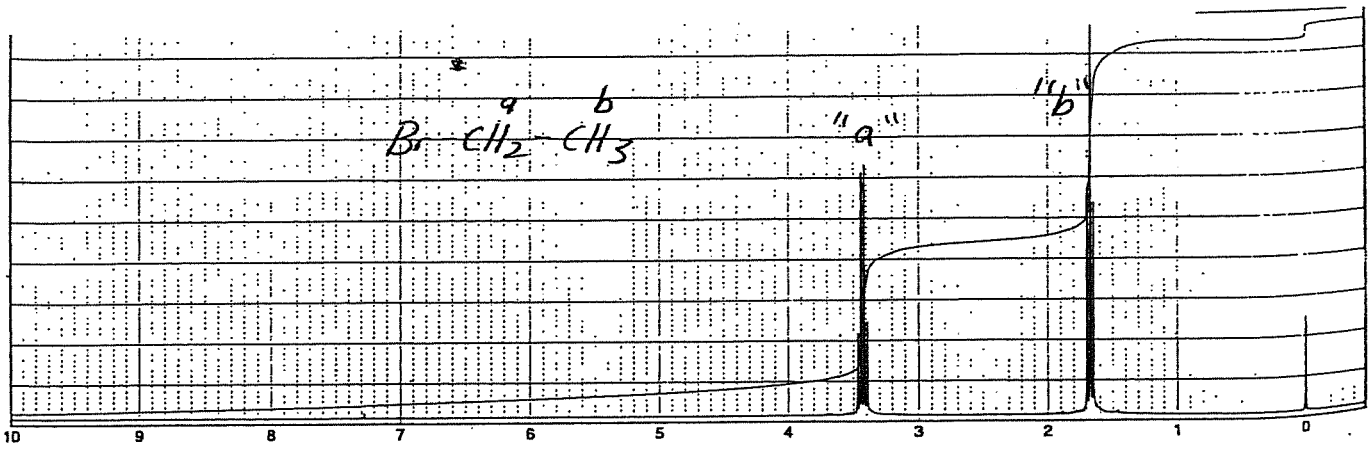
methane



bromoethane

Now consider a hydrogen near a halogen as in bromoethane. This type of hydrogen is in a magnetically altered situation as compared to the hydrogen in methane. The halogen atom has the effect due to its inherent electronegativity of pulling sigma electron density away from the hydrogens in the molecule. The effect is largest for the hydrogens closest to the halogen atom. Though the little local opposing sigma field is still generated next to the hydrogens, it is partially pulled away by the electronegative bromine . Therefore, the hydrogens experience less of the local field and more of the external field. In other words, the vector in the vicinity of the hydrogen has been reduced as compared to methane. After you do the vector addition you end up with a larger overall field (again as compared to methane). So going back to the fact that field and frequency are directly proportional, hydrogens near an electronegative atom should require a higher frequency to flip from the alpha to beta orientation. Therefore, they should appear at a higher PPM in the spectrum.

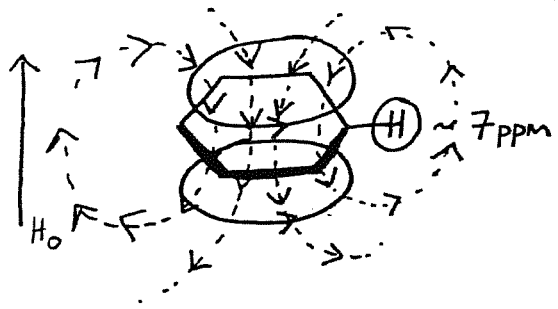
Hydrogens like those in bromoethane should appear from ca. 2.5-4.0 PPM in the NMR spectrum.



^1H NMR Spectrum of Bromoethane

Now as a last example, let us consider the NMR spectrum of benzene. Benzene and aromatics in general are very interesting because their hydrogens appear around 7 PPM even though they have no electronegative atoms. Why is this so? It has to do with the pi electrons. Because benzene and its relatives are aromatic, the p orbitals at each carbon in the ring overlap forming one continuous pi system. When the benzene ring is placed in a magnetic field, the external field induces a current in the pi system and that current generates a secondary magnetic field. **Once again remember that electric currents have associated magnetic fields and that magnetic fields generate currents.** The secondary magnetic field is such that it adds to the external field in the vicinity of the aromatic hydrogens as diagrammed below.

Benzene

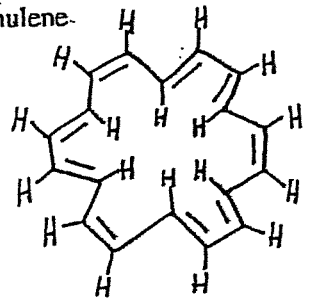


If the local field is in the same direction as the external field, the resulting field is larger than the external field. This means that the frequency needed to flip those hydrogens experiencing that field is larger. Larger frequency translates into higher PPM position.

It is really interesting to consider 18-annulene diagrammed below. 18-Annulene is a large enough ring to have both cis and trans double bonds. This means that some of the hydrogens are pointing in toward the center of the aromatic ring. Reconsider the diagram of benzene above. If you look at it carefully you will see that the magnetic field opposes the external field on the inside of the ring!!! If 18-annulene is aromatic like benzene, the

inner hydrogens should absorb at lower frequency (PPM) and guess what they do - they appear at -1.9 PPM!! Isn't that neat!!

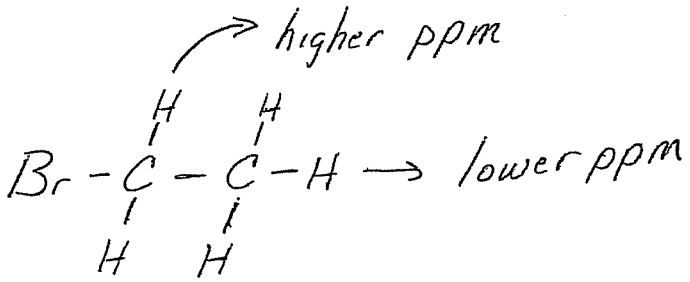
[18]Annulene



So summing up, the different hydrogens of a molecule appear at different positions because small local magnetic fields are generated when local electrons begin to circulate due to the effect of the external magnetic field. These small fields either add to or subtract from the external field altering the frequency needed for excitation. Some of the effects are due to the circulation of sigma electrons while others are due to the circulation of pi electrons. The pi effects can be the most dramatic as was demonstrated in the preceding examples.

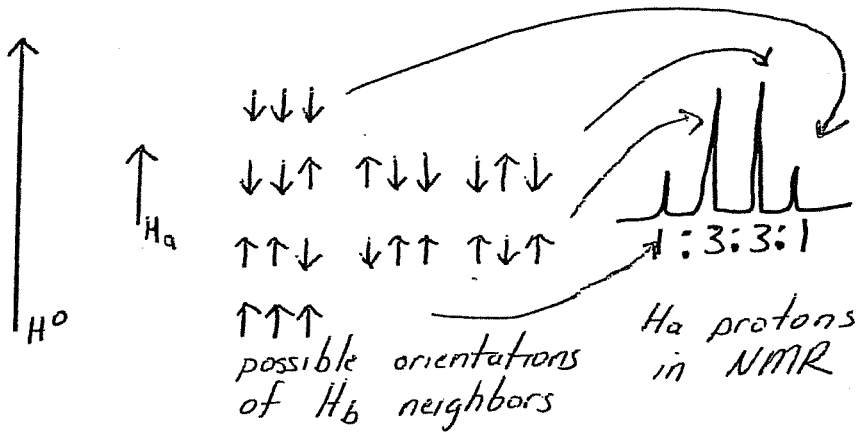
3. What causes splitting?

Many peaks in NMR spectra appear as symmetric patterns called doublets, triplets, quartets, quintets, etc. When you see these patterns it tells you about the number of adjacent (usually on the carbon next door to that bearing the absorbing hydrogen(s)), but different hydrogens. In simple spectra such as those we will be studying in organic chemistry lab, the number of peaks you see is one more than the number of adjacent, but different hydrogens. This is the so called **n+1** rule. Different means that the adjacent hydrogens have a different environment and absorb at a different frequency than the hydrogens in question. For example, consider bromoethane (structure given below).



Bromoethane has two different types of hydrogens so we expect two absorptions in the NMR spectrum. One absorption corresponds to the two hydrogens that are closest to the halogen atom. The other to the hydrogens comprising the methyl group that is farther away. Based on what I described above with regard to chemical shift (the PPM value), the hydrogens nearer the bromine should be at a higher PPM position. The hydrogens further from the bromine should be at lower PPM position.

Anyway, getting back the splitting, the hydrogens closer the bromine will appear as a quartet because they are near three different hydrogens (the hydrogens on the methyl group). Those adjacent hydrogens are communicating their presence to the hydrogens being flipped. They are saying "We are your neighbors and there are three of us." The reason they are able to communicate their presence is that they are little magnets and as such, they either add to or subtract from the external magnetic field depending on their orientation. Since there are many protons in a sample, the following are the possibilities for the neighboring hydrogens during excitation:



Please note that in the above diagram the "a" hydrogens are the ones near the bromine being flipped from the alpha to beta orientation. The "b" hydrogens are the three neighbors. As shown above, it is possible that a given "a" hydrogen will have three "b" hydrogens nearby that are aligned with the applied field during excitation. It is also possible that the three neighbors could be all aligned against the applied field. More probable is that either two protons will be aligned against the field or two with the field. These combinations are more probable because there are more combinations of the three nuclei that give rise to these two possibilities. Since there are three combinations of each of these two, they are each three times more probable than having all three adjacent nuclei aligned with or against the field.

Now let us think about what these neighboring, local magnets do to the overall field. The "a" hydrogens that have all three neighbors aligned against the field have a lower overall magnetic field. Going back to the fundamental nuclear magnetic resonance equation (see page 2), you would conclude that these "a" hydrogens would have a lower frequency requirement for the alpha to beta transition and therefore appear at lower PPM. For the "a" hydrogens having three neighbors with all three "b" hydrogens aligned with the external field, the cumulative local field adds to the external field. This resultant field is larger than the external field so higher frequency electromagnetic radiation is needed to induce the alpha to beta transition. For the "b" hydrogens near two nuclei aligned with the field and one nucleus aligned against the field there is a slight increase in overall field leading to slightly higher frequency requirements. Similarly, two spins aligned against and one aligned with the field leads to slightly lower frequency requirements. So in the end the "a" population is divided into four groups appearing at slightly different frequencies. The intermediate frequency peeks are taller than the higher and lower frequency peaks because they reflect more probable situations for local hydrogens. Hence a quartet is observed.

Now if you understand why the "a" hydrogens give a quartet can you figure out why the "b" hydrogens give a triplet? Try to work it out using vectors as done in the above diagram.

For simple systems like bromoethane, **n + 1** peaks will be observed for a given absorption, where n = the number of neighboring, but different hydrogens. This formula can be very useful when interpreting simple spectra.

The Interpretation of Simple NMR Spectra

This year we will abstract the following information from NMR spectra to determine structures of products from organic reactions and isolations.

1. The number of peaks. The number of peaks is directly related to symmetry. If a compound has three significantly different types of hydrogens, it should have three different NMR absorptions.

2. The area under each absorption (the integral). The relative areas (or integrals) of the various absorptions in an NMR spectrum equals the relative number of hydrogens absorbing. If we know the molecular formula of a compound, we can use this ratio to figure out the actual number of each type of hydrogen. From the numbers of each type, we can infer the carbon structure. For example, with bromoethane, the relative areas under the NMR peaks are 2:3. This tells us that there is a group of two hydrogens that are the same and another group of three hydrogens that are the same. With your current knowledge of organic chemistry, it seems most likely that the compound has a methyl ($-CH_3$) and a methylene ($-CH_2-$) groups. In other words, the most probable way to have three identical hydrogens is on a methyl group. The most probable way to have two identical hydrogens is in a methylene group.

Suppose you have a compound with the formula $C_5H_{12}O$ and you are told that there are two NMR peaks, having the relative areas of 1:3. Can you come up with the structure of the compound?

3. The splitting pattern. For this semester, we will be using the **n+1** rule as it applies to the simple structures we will be determining. You will see one more peak than the number of adjacent, but different hydrogens. Therefore you can look at any peak and automatically know how many neighbors there are. This is crucial information because it allows you to start to hook atoms together in your structure. The problem is that people often confuse integral with splitting. So you must always remember **"Integral tells you what is here and splitting tells you what is near"** This means that the integral tells you about the absorbing hydrogens and the splitting tells you about the neighbors. So what does it mean if you see a quintet with an area of two in a spectrum?

4. The position of the peak or the chemical shift (δ). This tells you about the electronic environment (the electronic environment directly relates to the magnetic environment) of the absorbing hydrogens. It will tell you if there are pi bonds or electronegative atoms nearby, etc. There are nice tables available that organize how different groups effect the frequency of absorptions and in lab you will always have these tables available to you. Yes, you will even have them on exams. A good rule of thumb when you are solving spectra is that the closer a hydrogen is to an electronegative atom the higher the PPM position. This little rule only works if the hydrogen is two or more bonds away from the atom. You will soon see the utility of this when you begin your problems today. It is also useful to keep in your head that aromatic hydrogens absorb at around 7 PPM.

A few tricks of the trade that are generally useful for spectral problem solving.....

1. Always calculate the index of hydrogen deficiency or unsaturation number at the beginning of a problem (you will normally be given the formula of the compound). Determining the unsaturation number is very helpful in regard to knowing which structural elements need to be present in your final solution. The unsaturation number is where you

compare the actual formula with the theoretical saturated formula and compute the number of pairs of hydrogens that are missing. This topic should have been covered in class by now.

2. It is a good idea to interpret your IR spectrum before you do the NMR spectrum so that you have an idea about which functional groups are present in your molecule.

3. Organize your ideas about the structure of the unknown as you go along. For some people it is helpful to set up the following table for the NMR data and conclusions. The important part of the table is the conclusion column in which you are drawing a structural conclusion about the absorbing hydrogens and their neighbors. You should write a structural fragment down as has been done below for bromoethane.

ppm δ	integral δ	Splitting	Conclusion
1.6	3	triplet	CH_3-CH_2-
3.4	2	quartet	-CH_2-CH_3 ↳ near electronegative atom

4. You will notice as we do problems in class that we tend to emphasize and draw the most information from the integral and splitting. Chemical shift (PPM position) in many cases is the last point of interest. There are a few relevant chemical shifts that should be interpreted immediately. One is the aromatic chemical shift. Aromatic hydrogens absorb at ca. 7 PPM. This is a very distinct and characteristic shift and should be interpreted immediately. If you observe a peak at seven chances are you have an aromatic ring. The most common aromatic ring is benzene. Another very distinctive shift is that of the aldehyde functional group. Aldehydic hydrogens appear at ca. 9 PPM in the spectrum. If you see a shift of nine PPM assume that you have an aldehyde functional group.

5. Solving spectra rapidly involves making good educated guesses. If you get an integral of three there is really only one probable way to have three identical hydrogens - a methyl group. If you get an integral of nine it is most likely three methyl groups that are the same by symmetry. If you get aromatic absorptions, you probably have one or more benzene rings. Always start with the simplest ideas and work your way toward more exotic solutions.

If you want to discuss any of these please feel free to stop by.

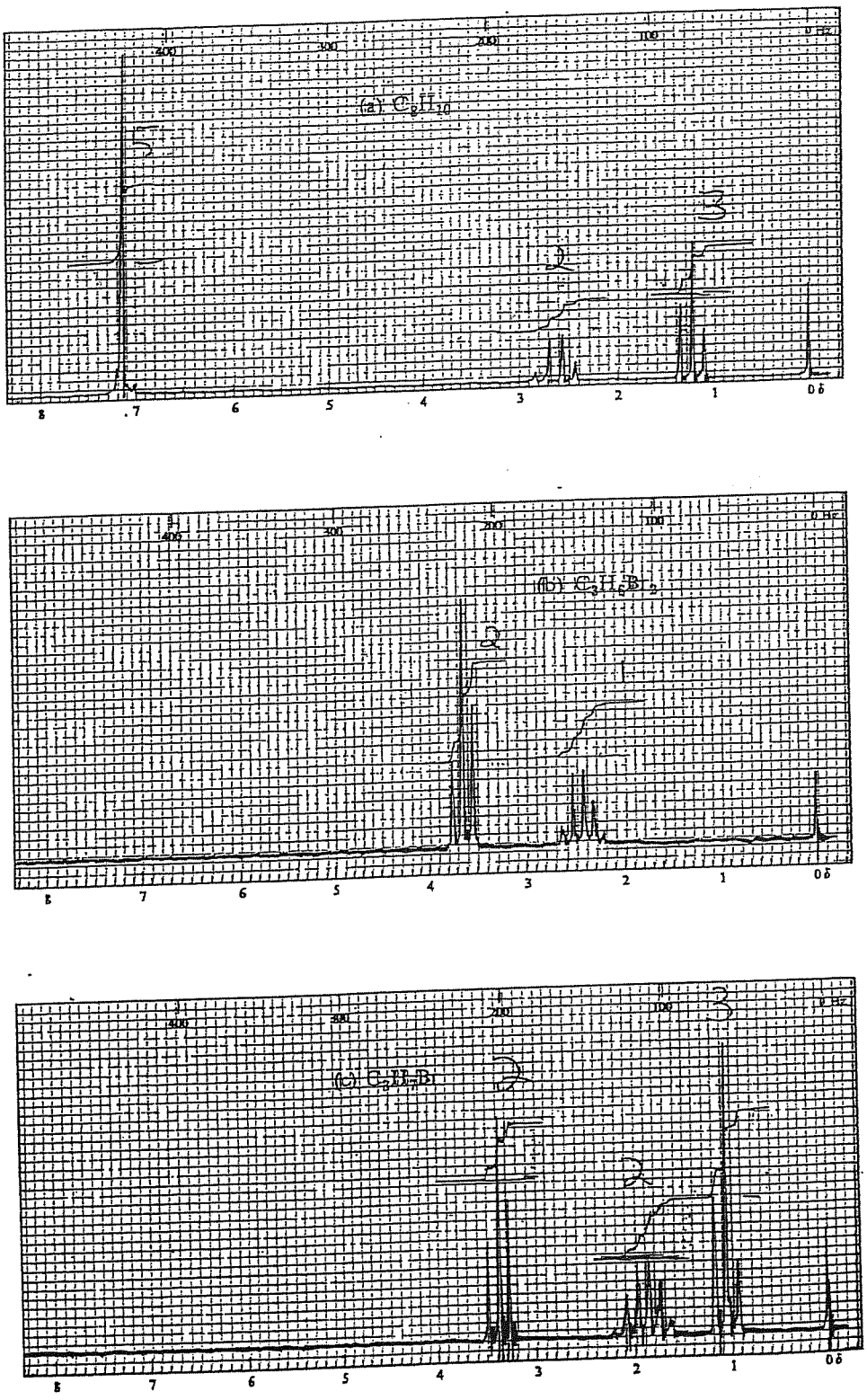


Figure 13.16. Nmr spectra for Problem 13.12, p. 435.

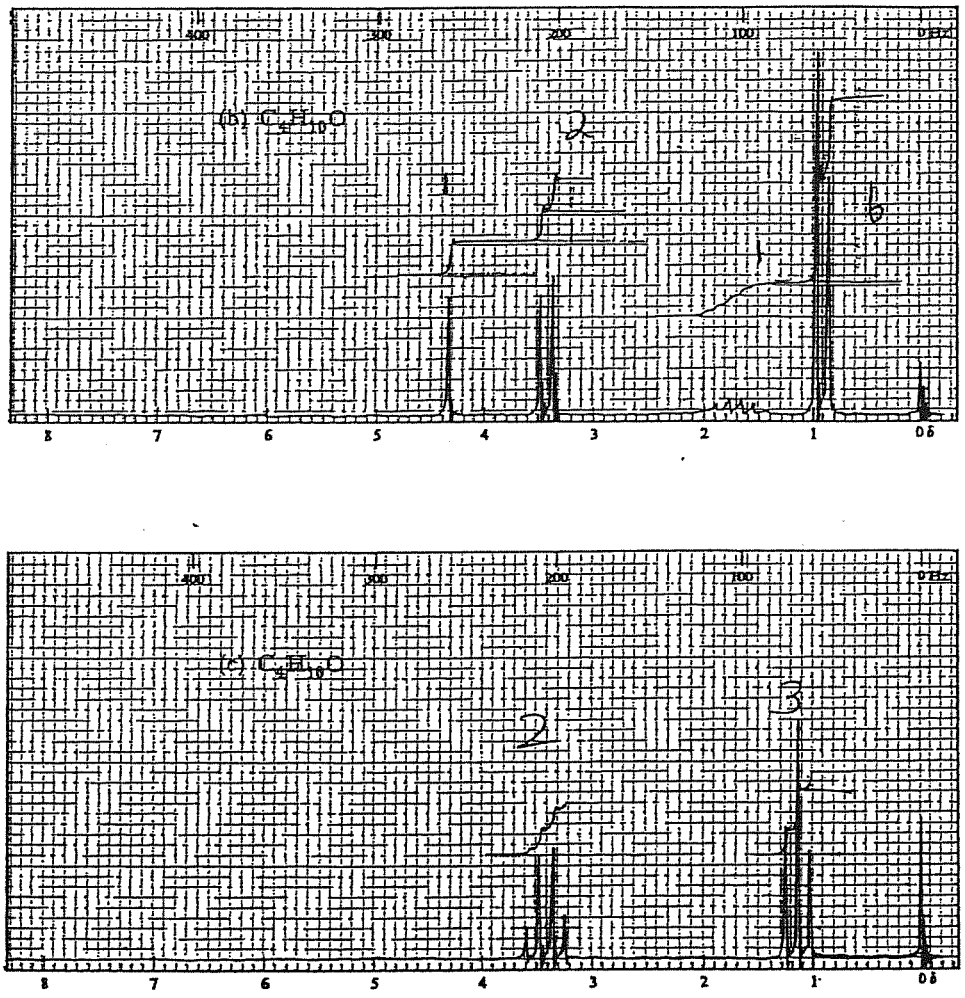


Figure 16.2. Nmr spectra for Problem 22, p. 546.

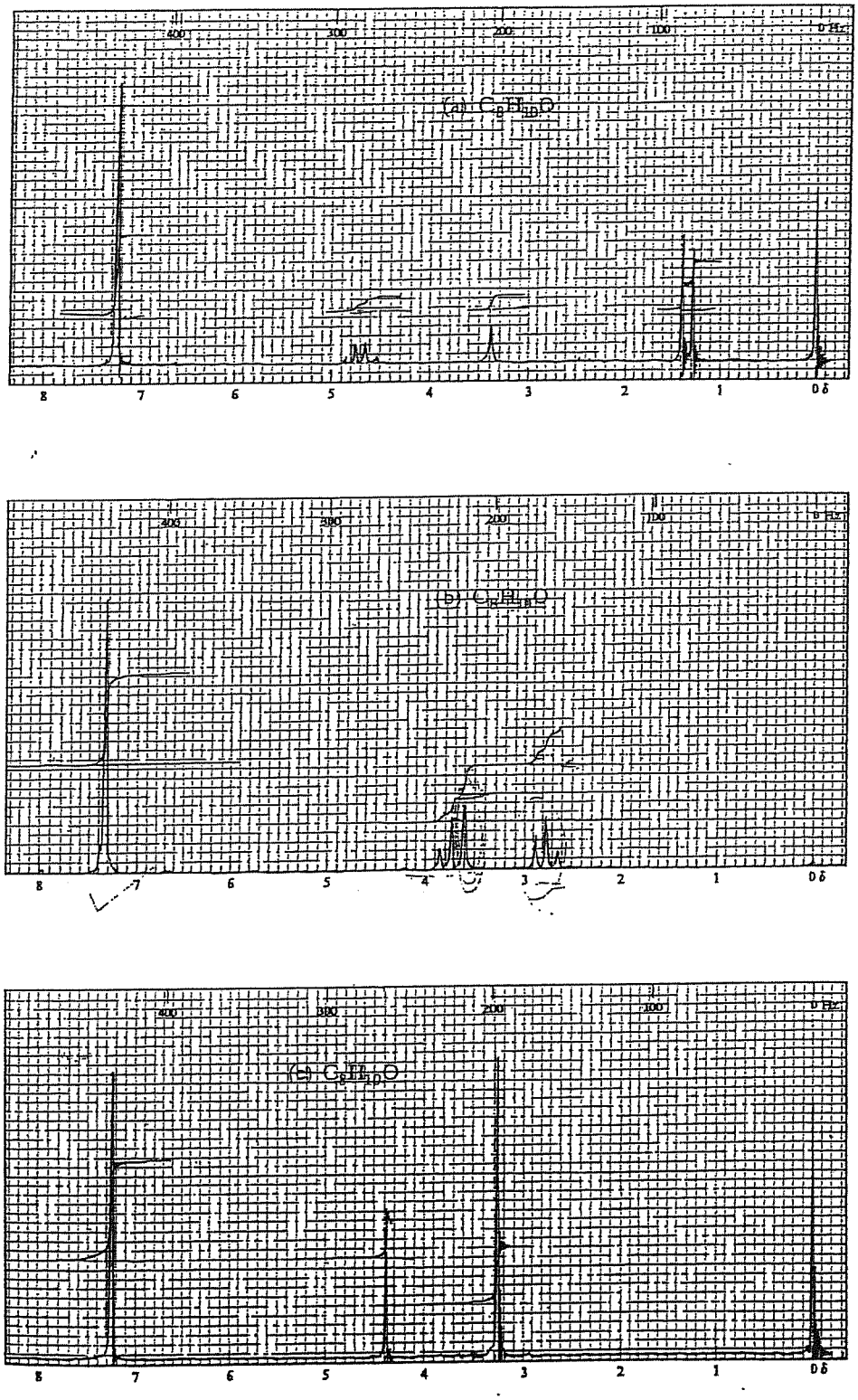


Figure 16.3. Nmr spectra for Problem 23, p. 546.

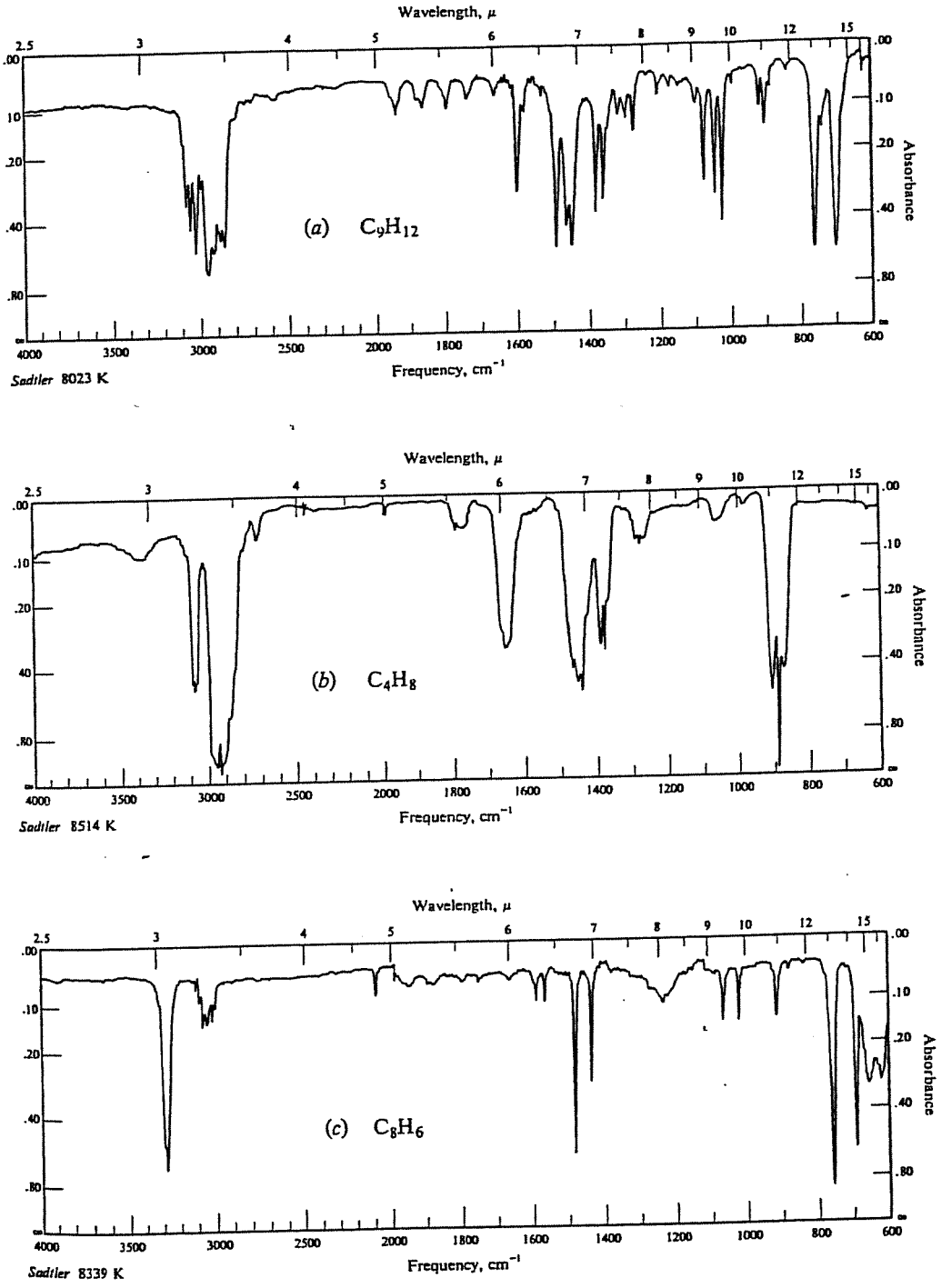
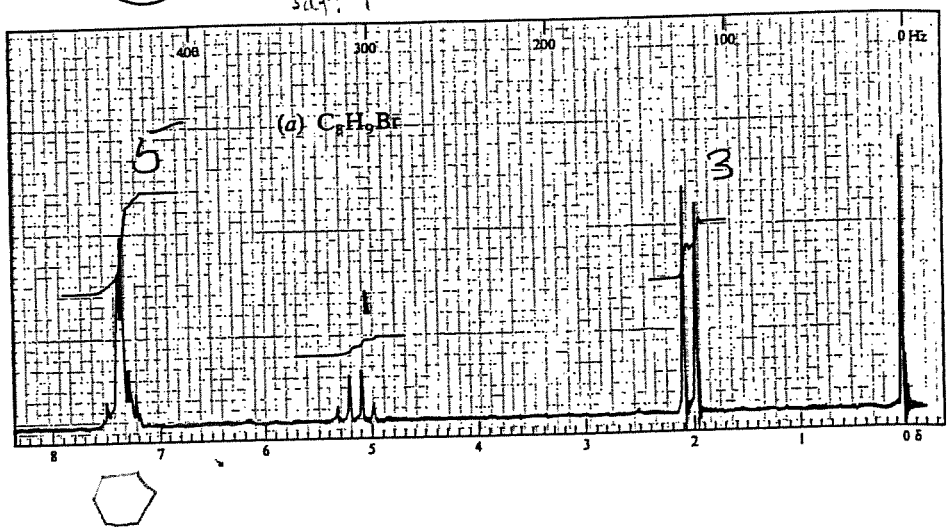
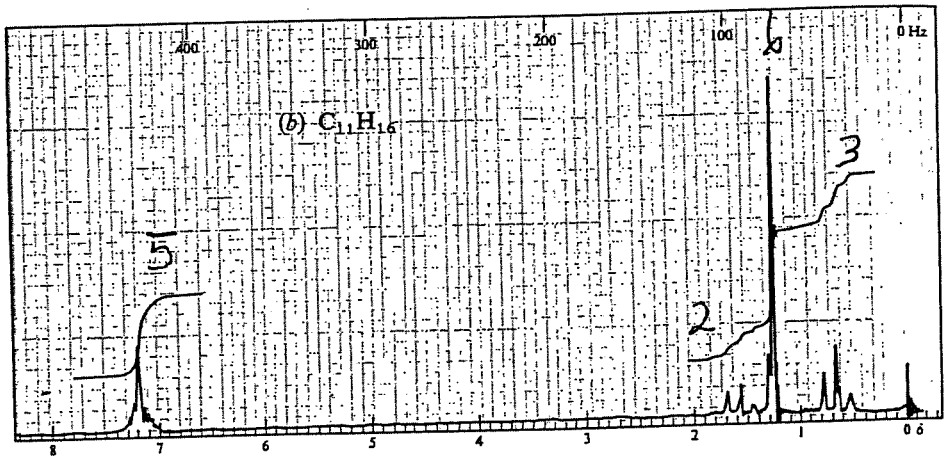


Figure 16.24 Infrared spectra for Problem 17, p. 623.





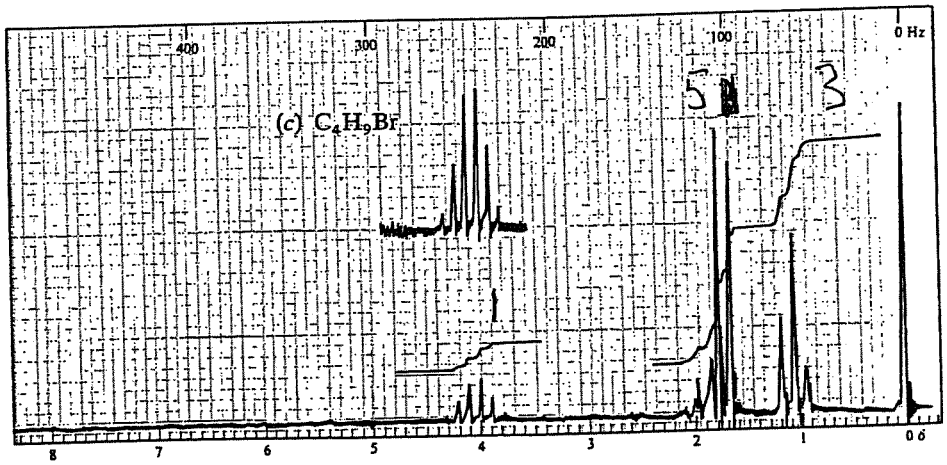


Figure 16.27 Proton NMR spectra for Problem 20, p. 624.

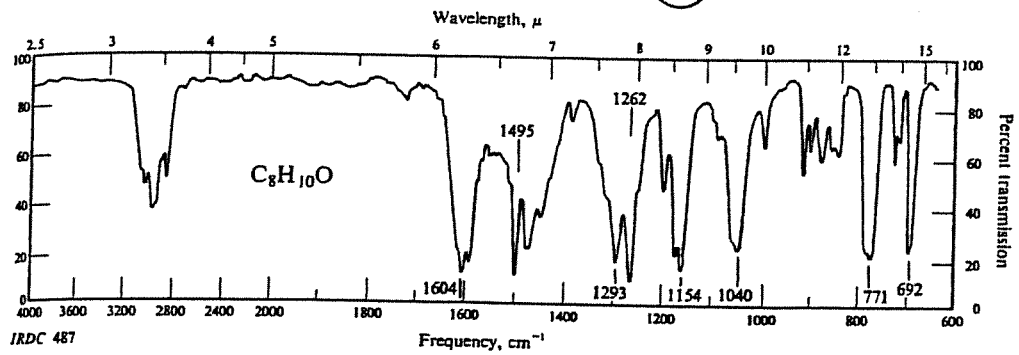
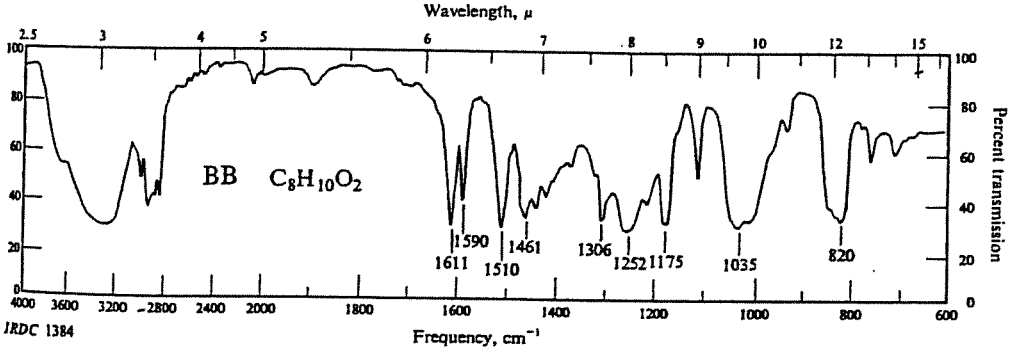


Figure 19.4 Infrared spectrum for Problem 16, p. 726.



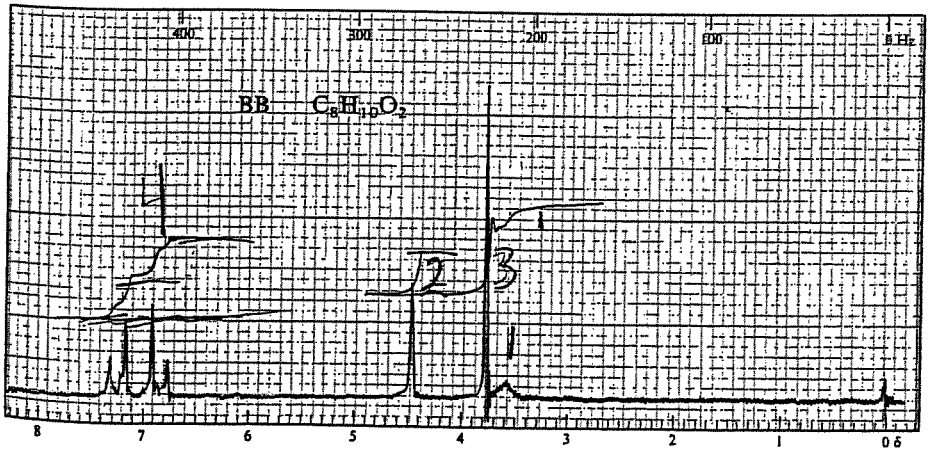


Figure 19.5 Infrared and proton NMR spectra for Problem 17, p. 726.

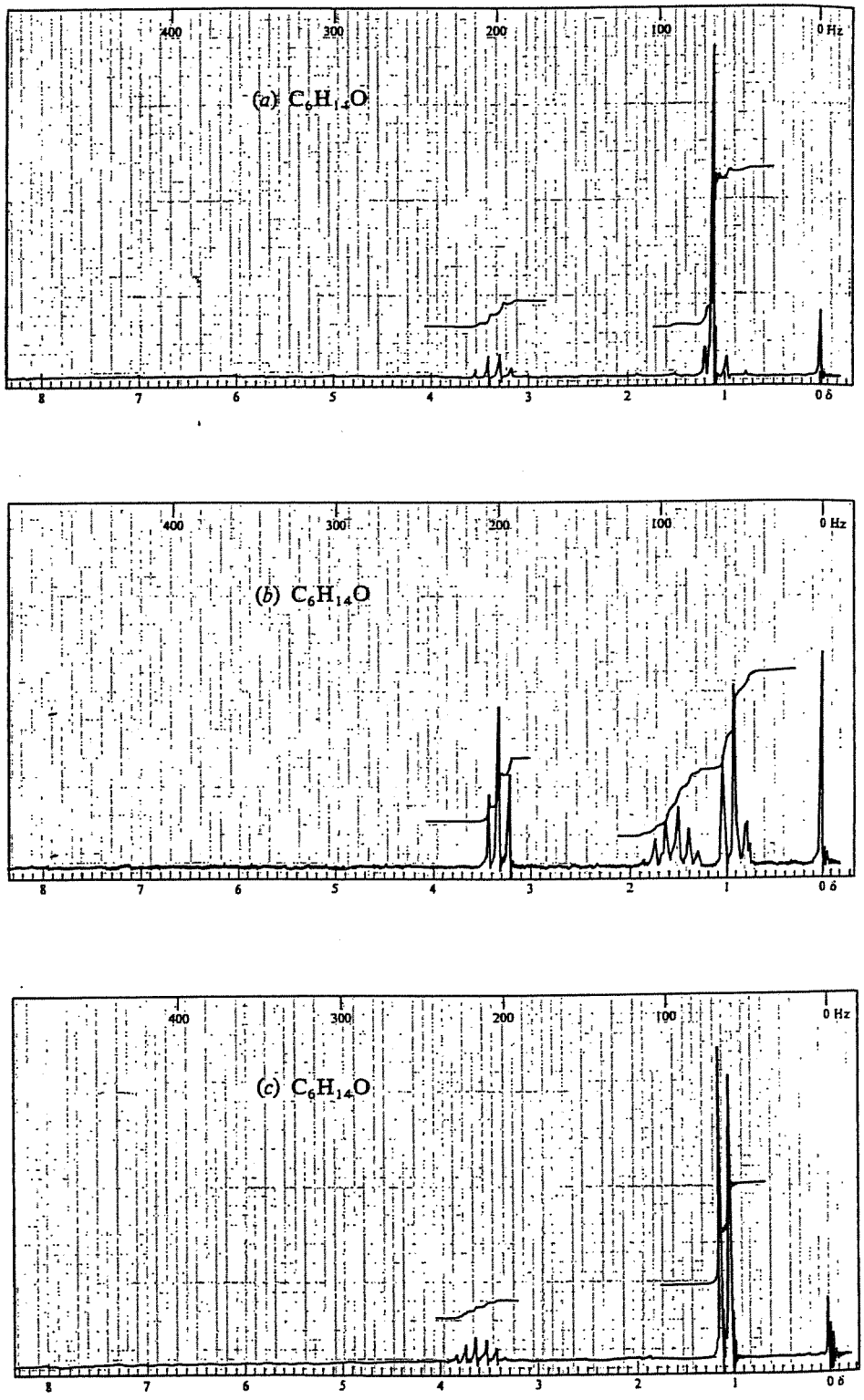
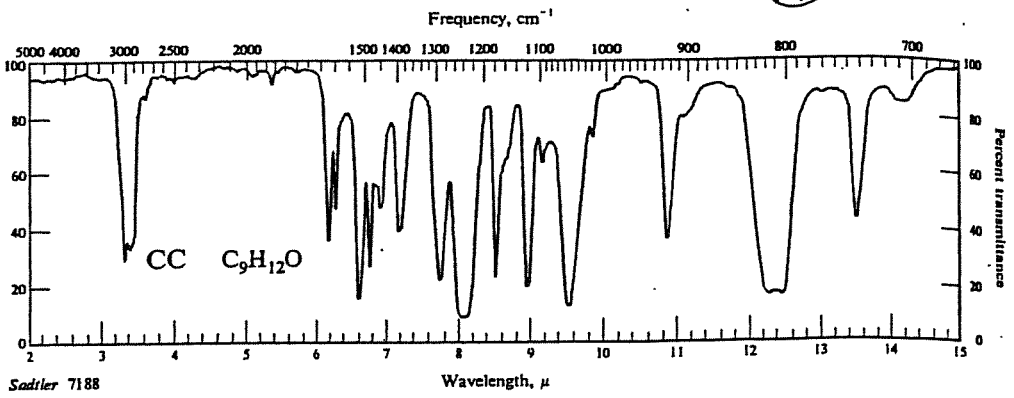
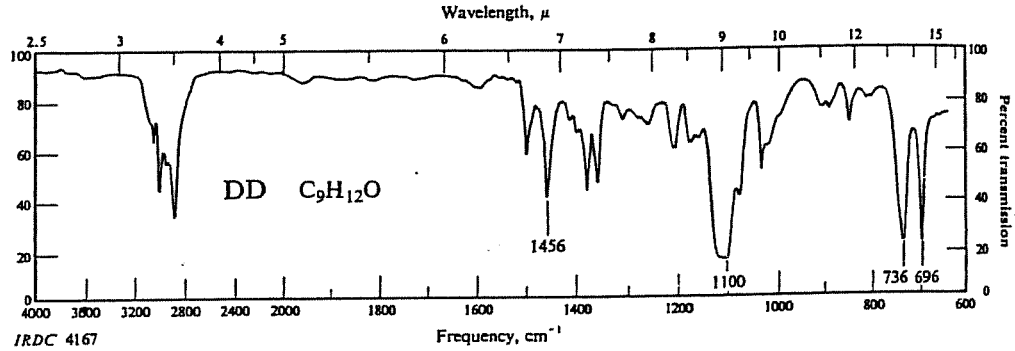


Figure 19.6 Proton NMR spectra for Problem 18, p. 726.





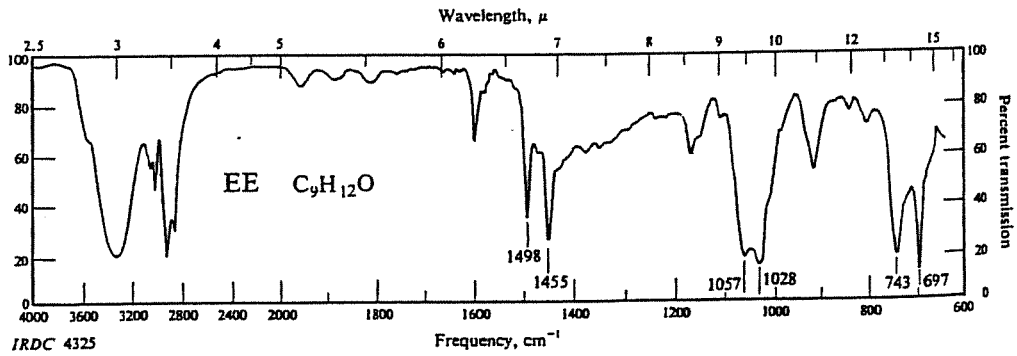
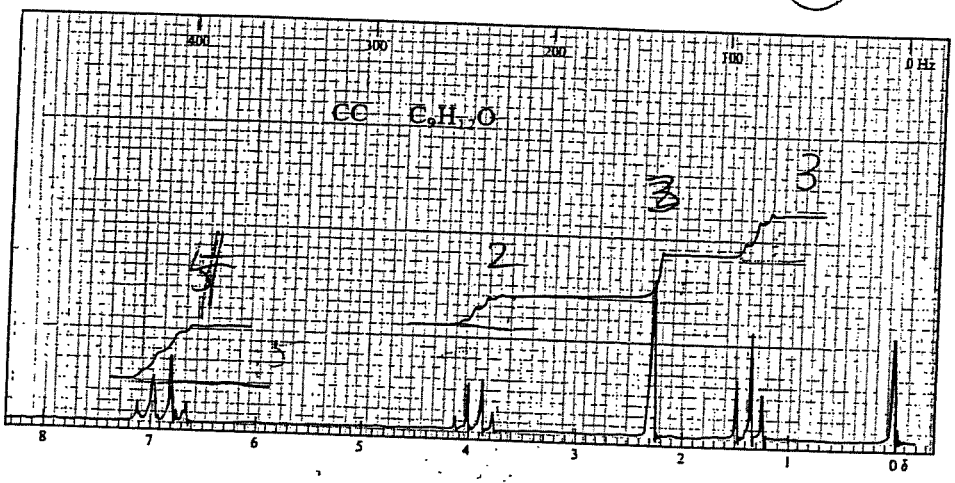
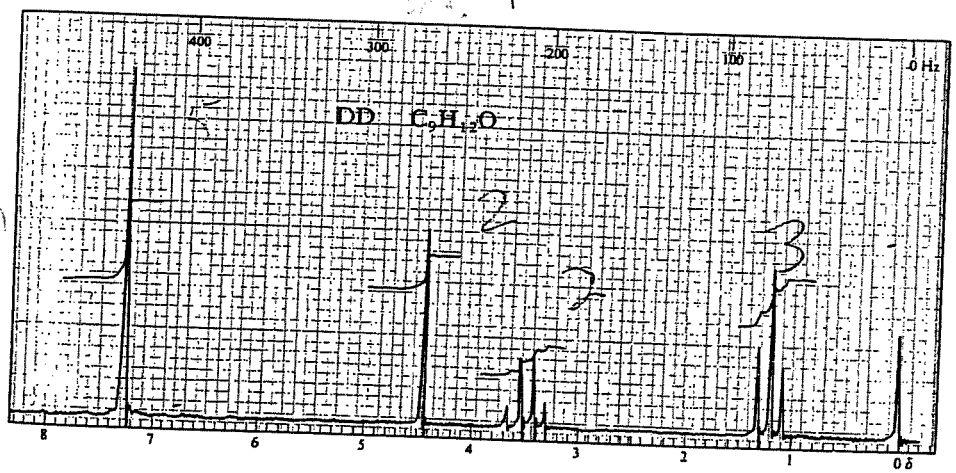


Figure 19.8 Infrared spectra for Problem 20, p. 726.





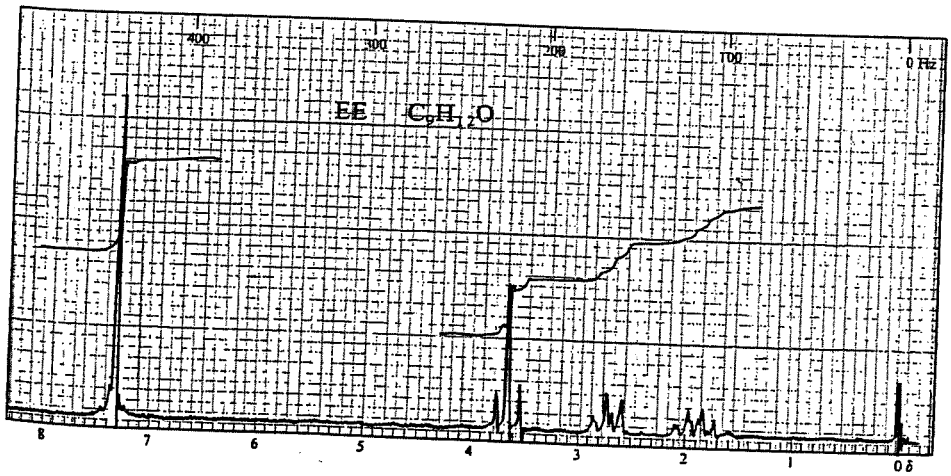
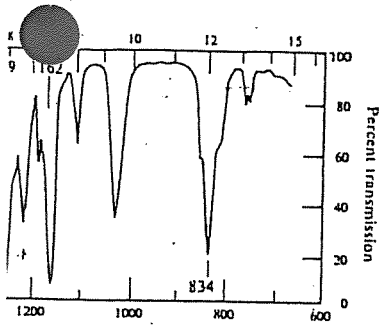
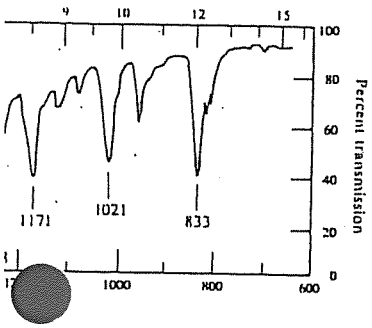
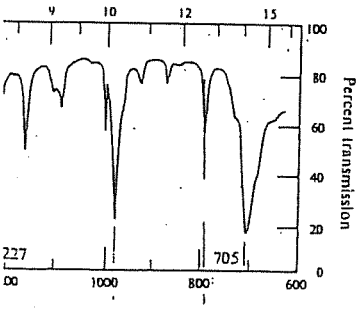
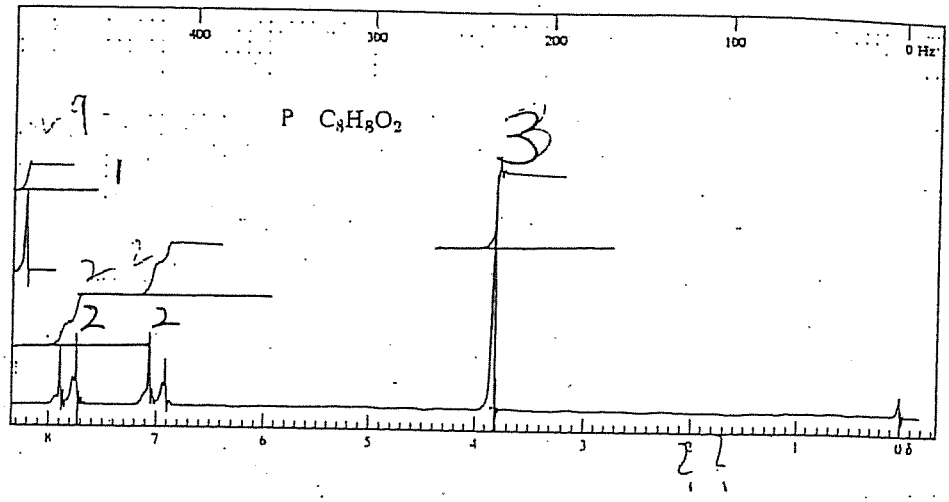


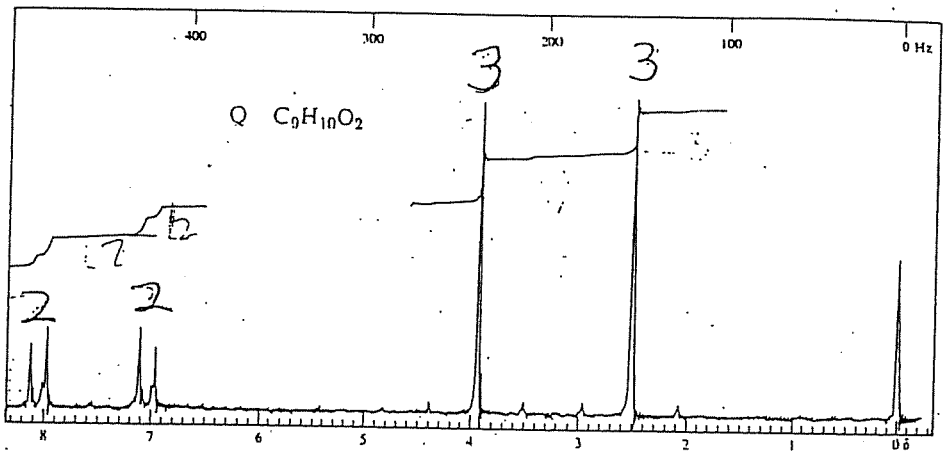
Figure 19.9 Proton NMR spectra for Problem 20, p. 726.

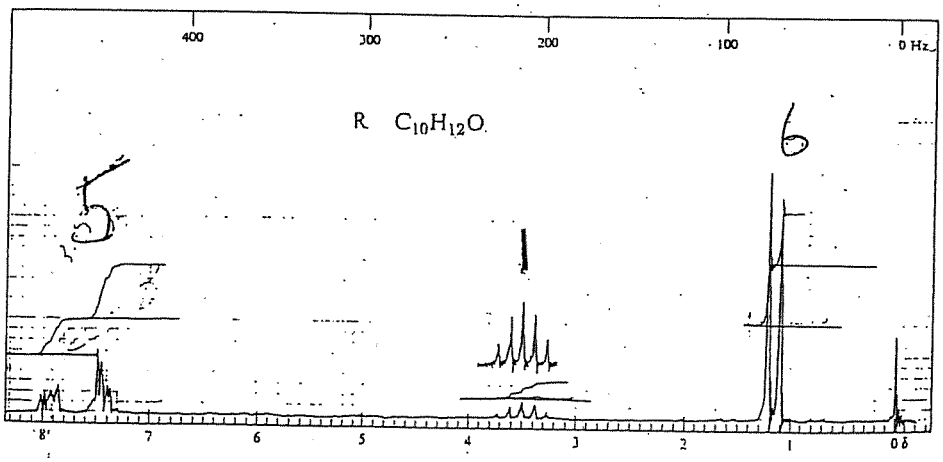








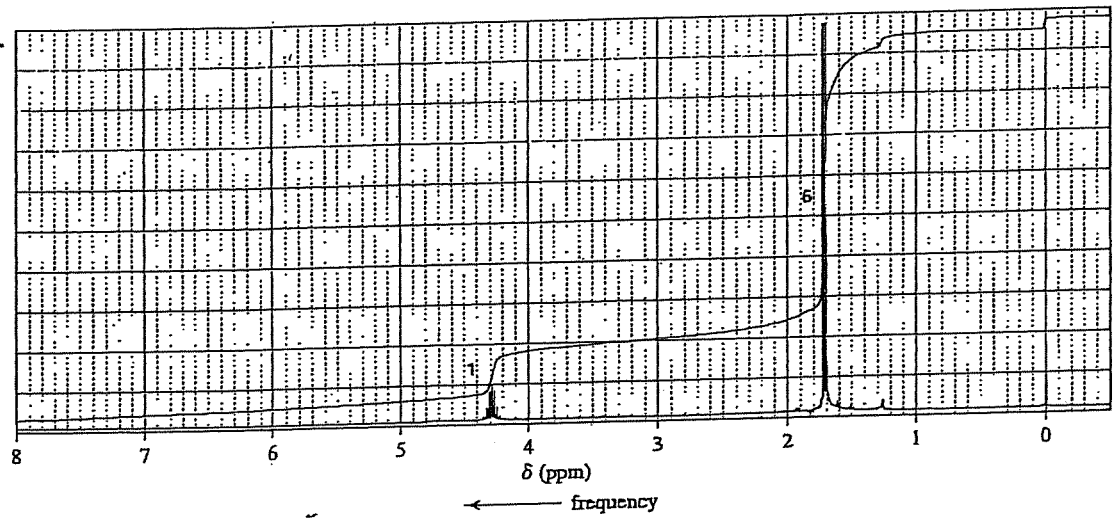




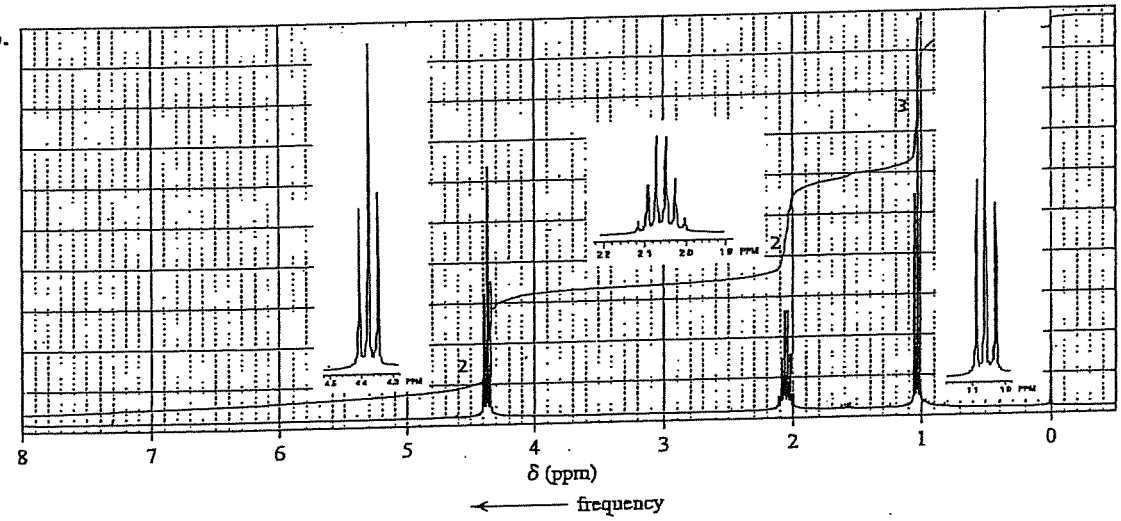
30, p. 653.

Figure 19.5. Nmr spectra for Problem 30, p. 653.

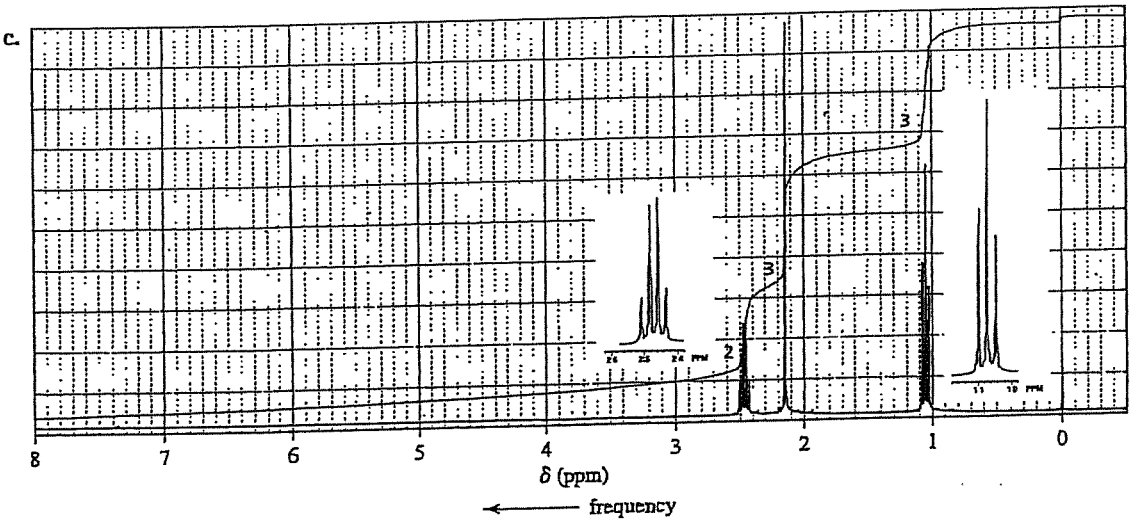
a.



b.

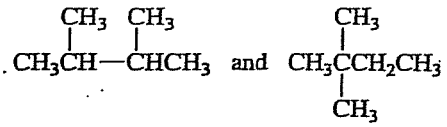


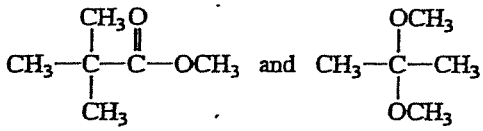
c.

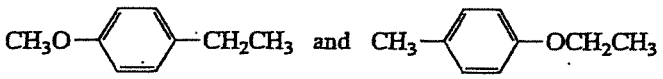


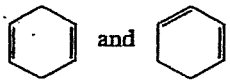
47. Determine the ratios of the chemically nonequivalent protons in a compound if the steps of the integration curves measure 40.5, 27, and 118 mm, from left to right across the spectrum. Give the structure of a compound whose ^{1}H NMR spectrum would show these integrals in the observed order.

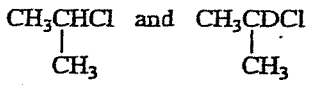
48. How could ^{1}H NMR distinguish between the compounds in each of the following pairs?
a. $CH_3CH_2CH_2OCH_3$ and $CH_3CH_2OCH_2CH_3$
b. $BrCH_2CH_2CH_2Br$ and $BrCH_2CH_2CH_2NO_2$

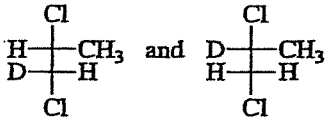
c. 

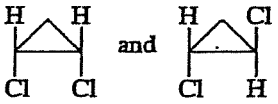
d. 

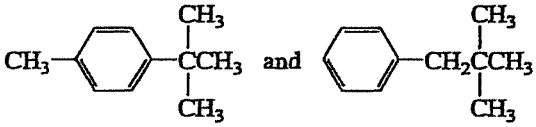
e. 

f. 

g. 

h. 

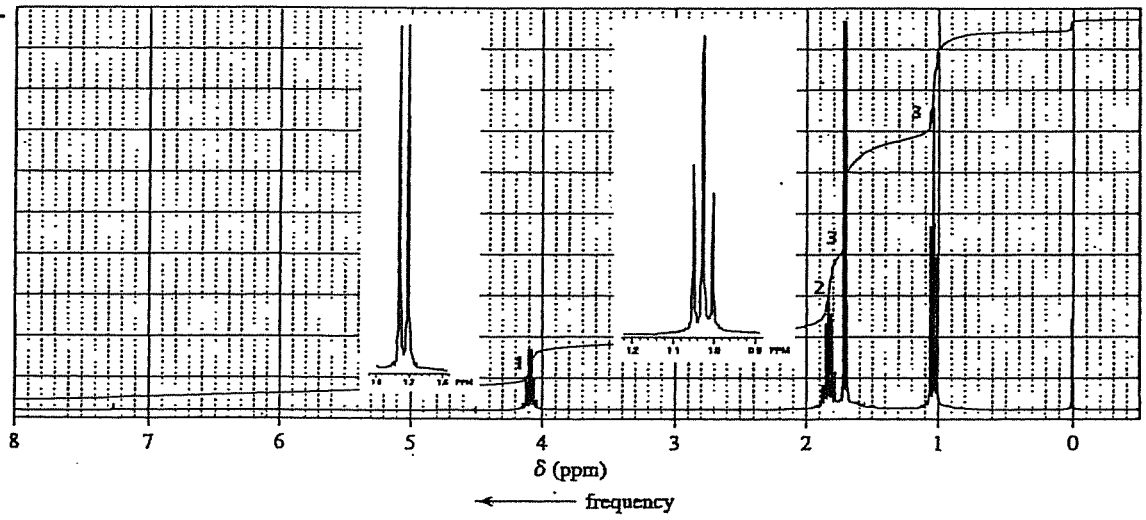
i. 

j. 

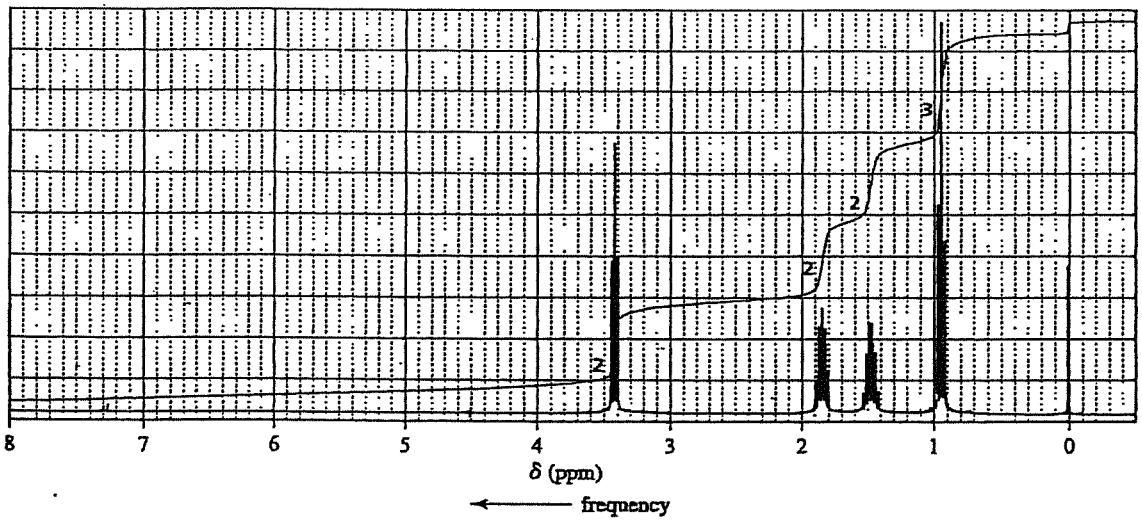
9. Answer the following questions:
   a. What is the relationship between chemical shift in ppm and operating frequency?
   b. What is the relationship between chemical shift in hertz and operating frequency?
   c. What is the relationship between coupling constant and operating frequency?
   d. How does the operating frequency in NMR spectroscopy compare with the operating frequency in IR and UV/Vis spectroscopy?

0. The ^{1}H NMR spectra of three isomers with molecular formula C_4H_9Br are shown here. Which isomer produces which spectrum?

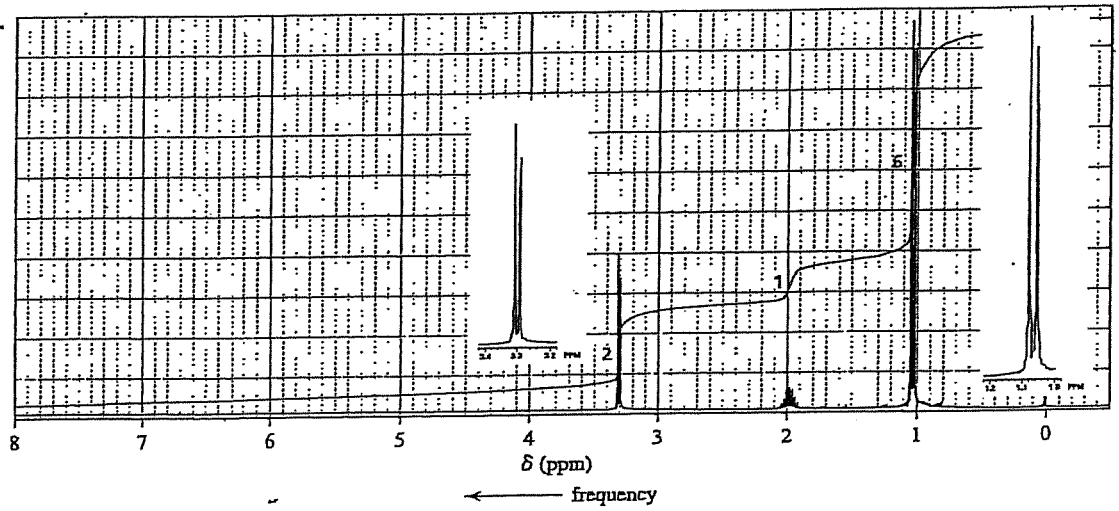
a.



b.



c.



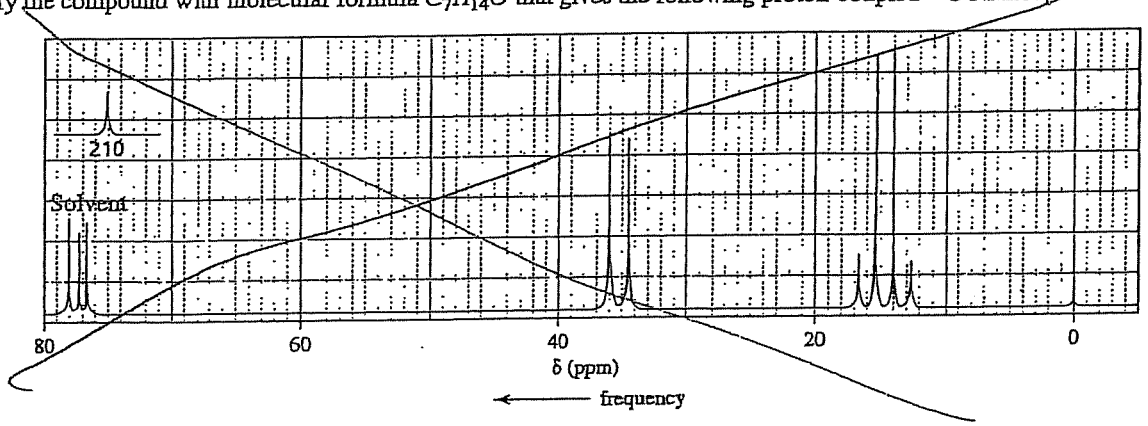
51. Identify each of the following compounds from the ^{1}H NMR data and molecular formula. The number of hydrogens responsible for each signal is shown in parentheses.

a. $C_4H_8Br_2$ 1.97 ppm (6) singlet
3.89 ppm (2) singlet

b. C_8H_9Br 2.01 ppm (3) doublet
5.14 ppm (1) quartet
7.35 ppm (5) broad singlet

c. $C_5H_{10}O_2$ 1.15 ppm (3) triplet
1.25 ppm (3) triplet
2.33 ppm (2) quartet
4.13 ppm (2) quartet

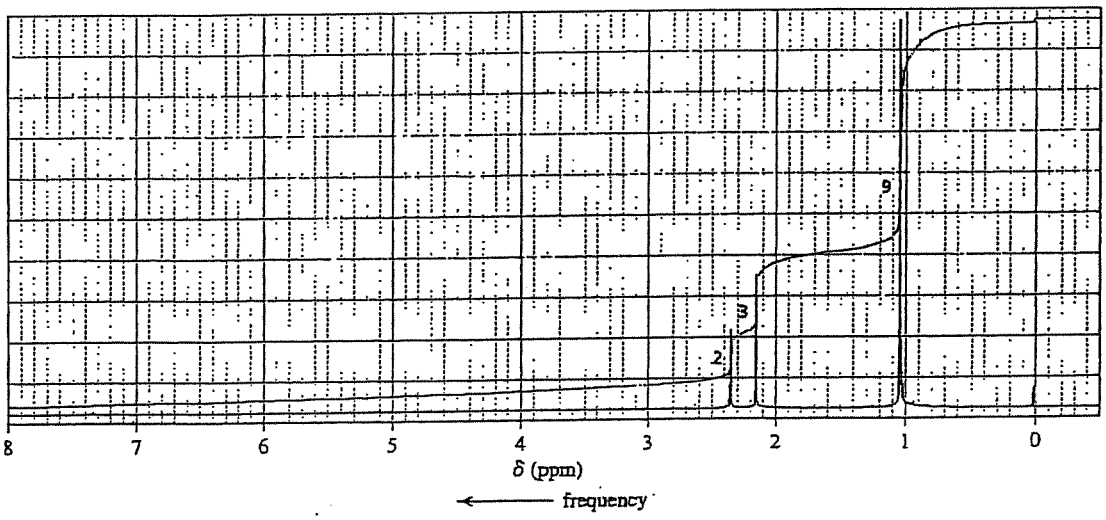
52. Identify the compound with molecular formula $C_7H_{14}O$ that gives the following proton-coupled ^{13}C NMR spectrum:



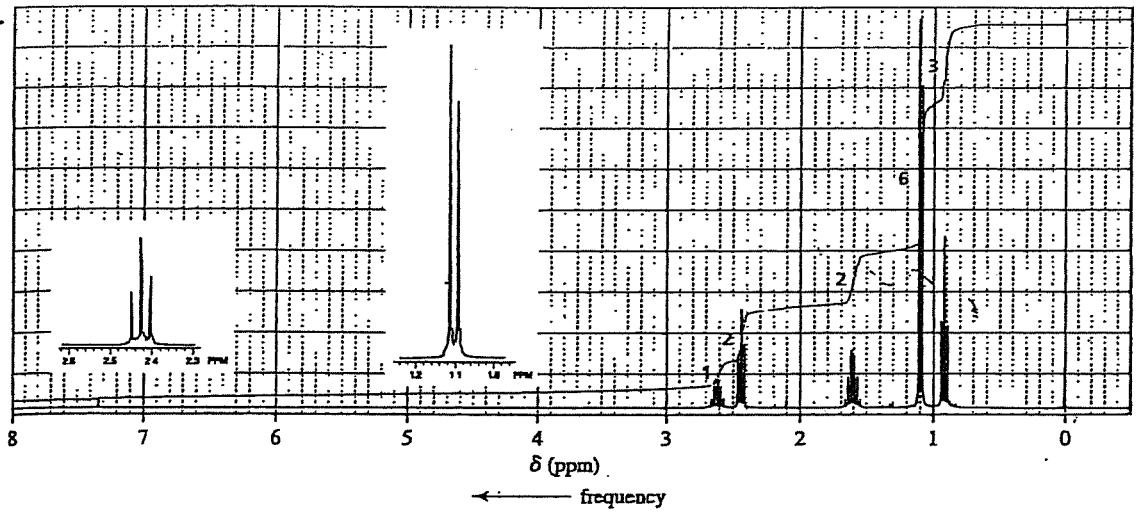
53. Compound A, with molecular formula C_4H_9Cl, shows two signals in its ^{13}C NMR spectrum. Compound B, an isomer of compound A, shows four signals, and in the proton-coupled mode, the signal farthest downfield is a doublet. Identify compounds A and B.

54. The ^{1}H NMR spectra of three isomers with molecular formula $C_7H_{14}O$ are shown here. Which isomer produces which spectrum?

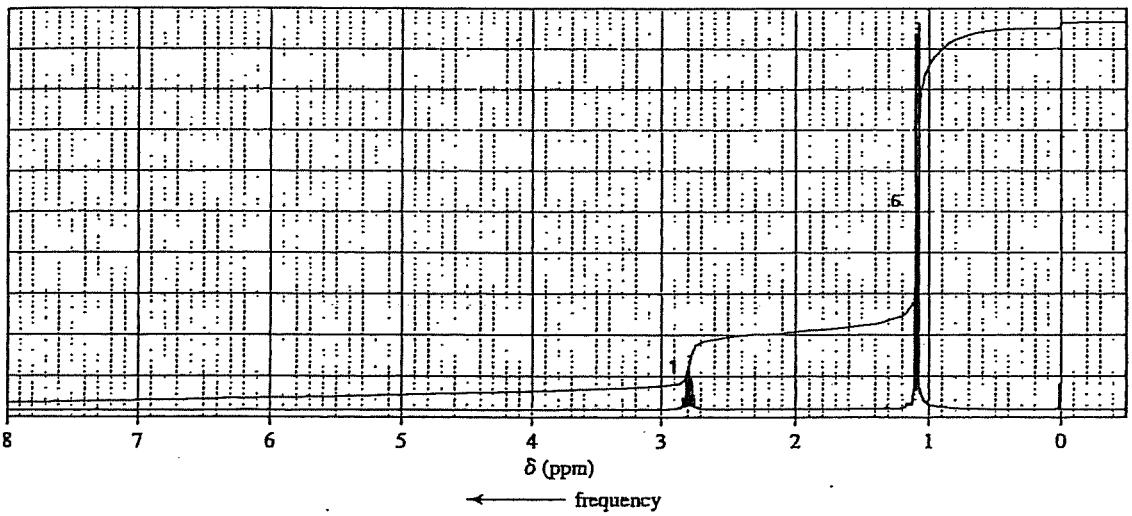
a.



b.



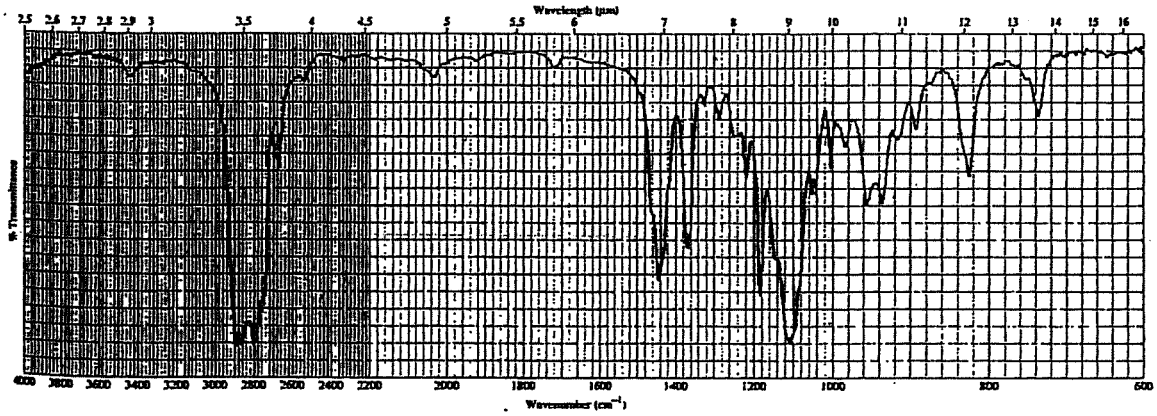
c.

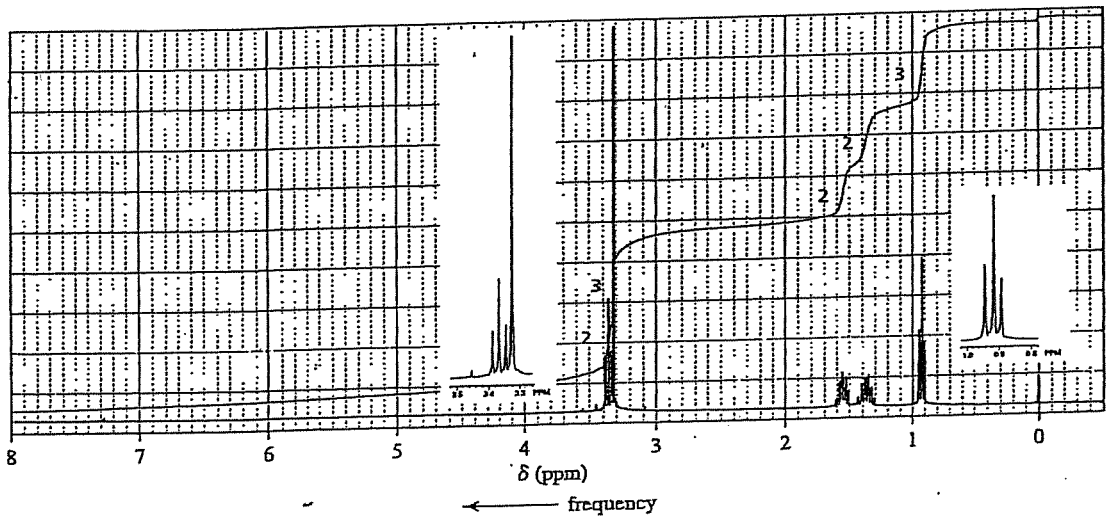


5. Would it be better to use ^{1}H NMR or ^{13}C NMR to distinguish between 1-butene, *cis*-2-butene, and 2-methylpropene? Explain your answer.

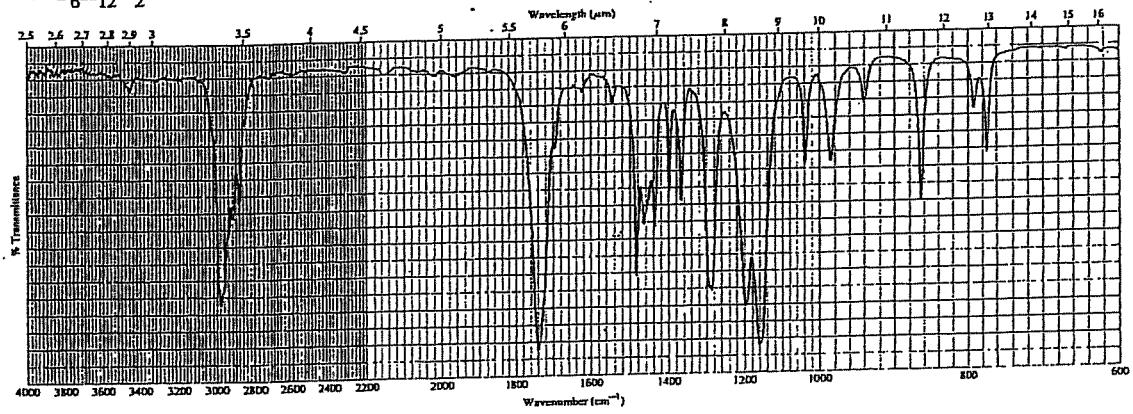
6. Determine the structure of each of the following unknown compounds based on its molecular formula and its IR and ^{1}H NMR spectra.

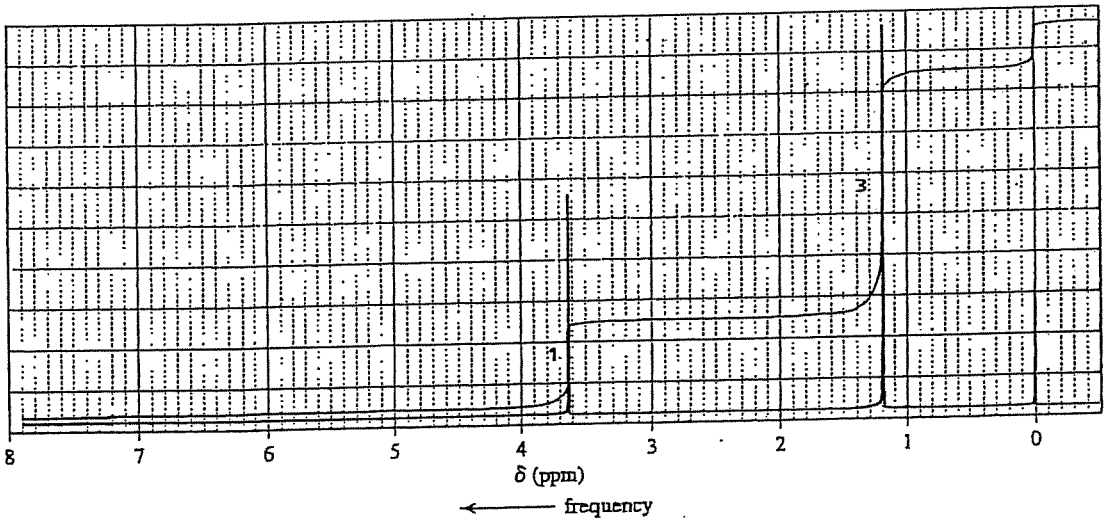
a. $C_5H_{12}O$



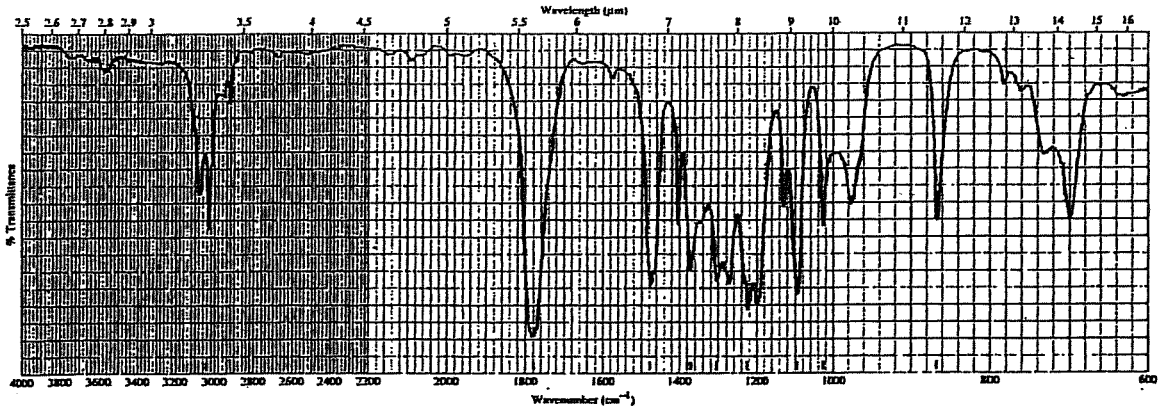

3
2
2
3
2
8
7
6
5
4
3
2
1
0
δ (ppm)
frequency

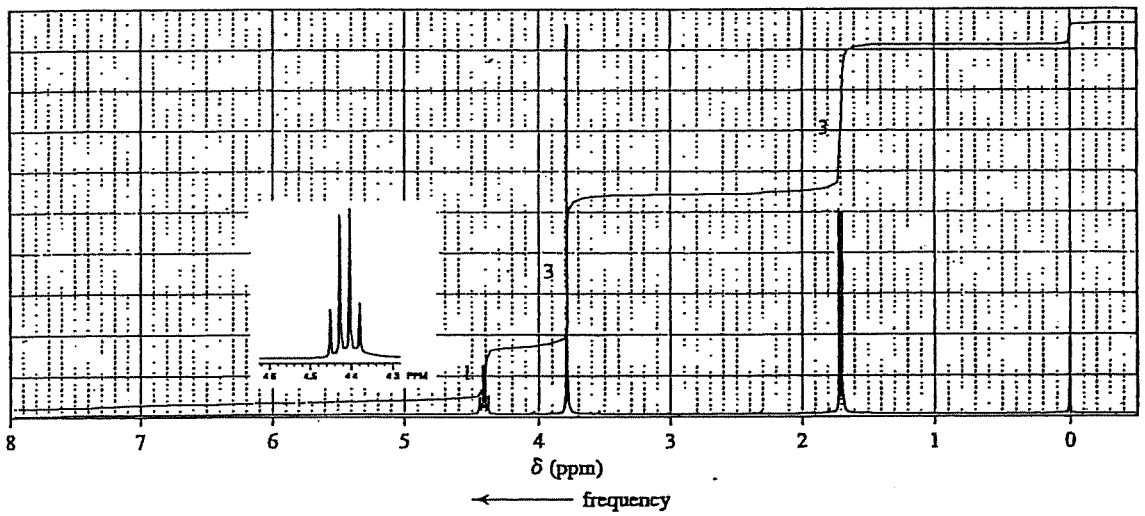
b. $C_6H_{12}O_2$


Wavelength (μm)
% Transmittance
4000 3800 3600 3400 3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600
Wavenumber (cm⁻¹)

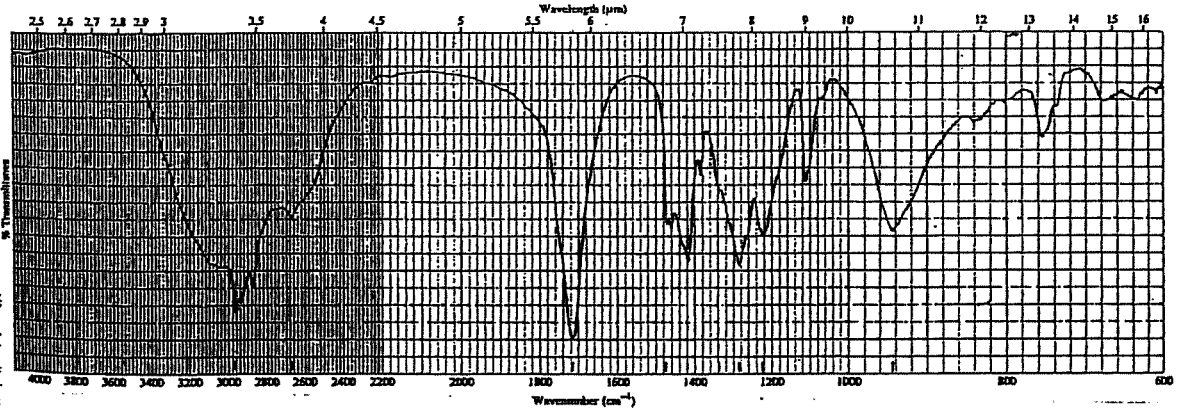

3
1
8
7
6
5
4
3
2
1
0
δ (ppm)
frequency

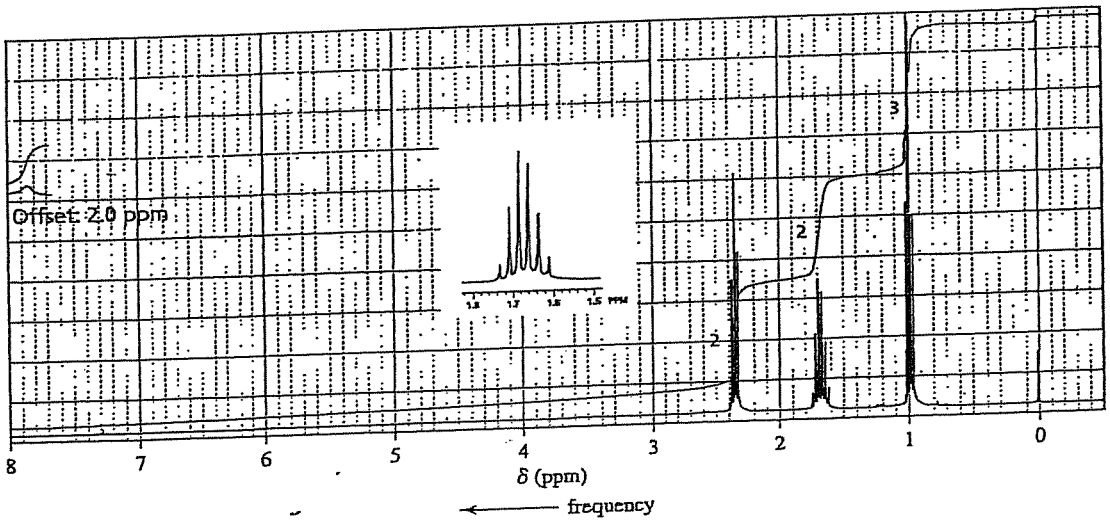
c. $C_4H_7ClO_2$





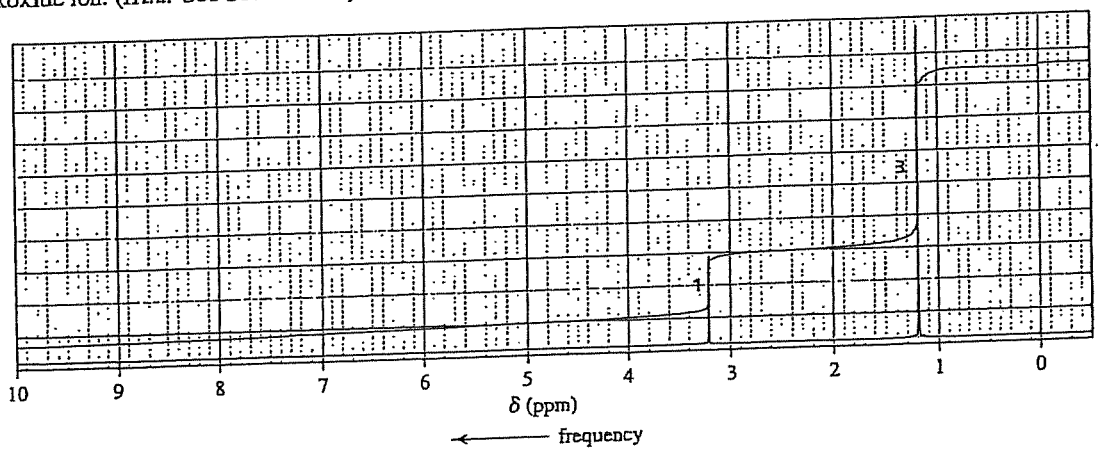
d. $C_4H_8O_2$





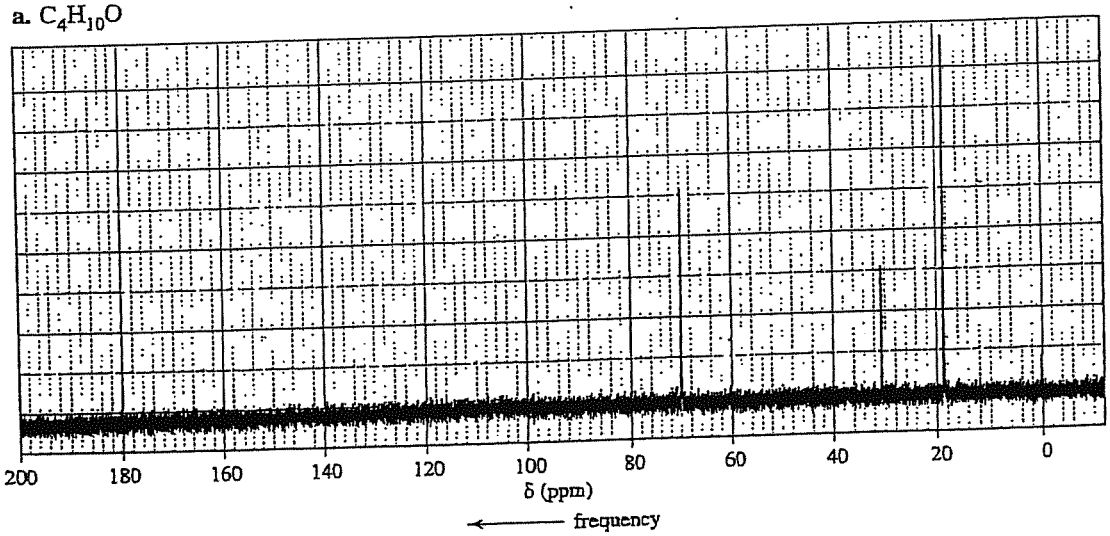
57. There are four esters with molecular formula $C_4H_8O_2$. How could they be distinguished by ^1H NMR?

58. An alkyl halide reacts with an alkoxide ion to form a compound whose ^1H NMR spectrum is shown here. Identify the alkyl halide and the alkoxide ion. (*Hint:* See Section 9.9.)

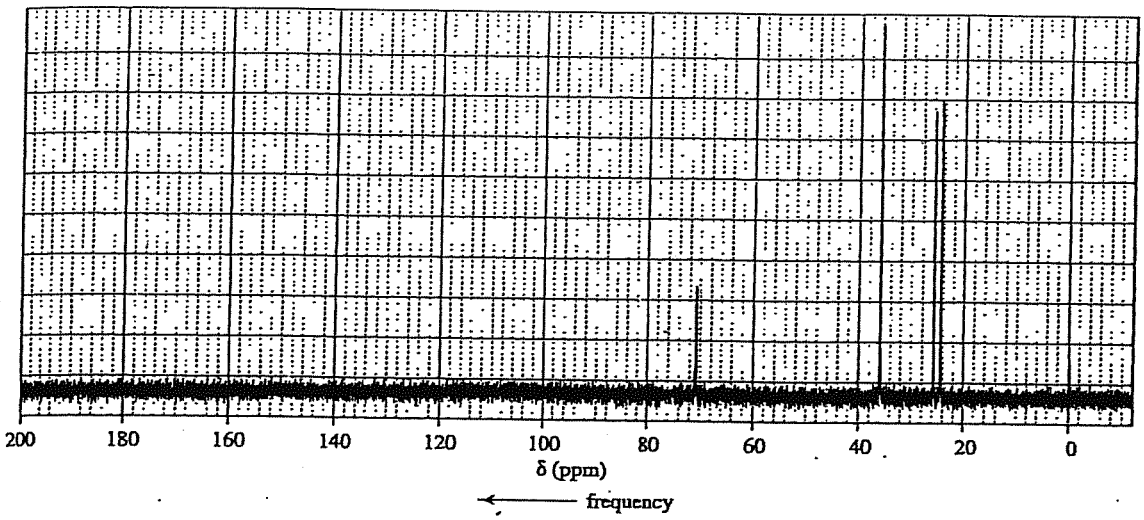


59. Determine the structure of each of the following compounds based on its molecular formula and its ^{13}C NMR spectrum:

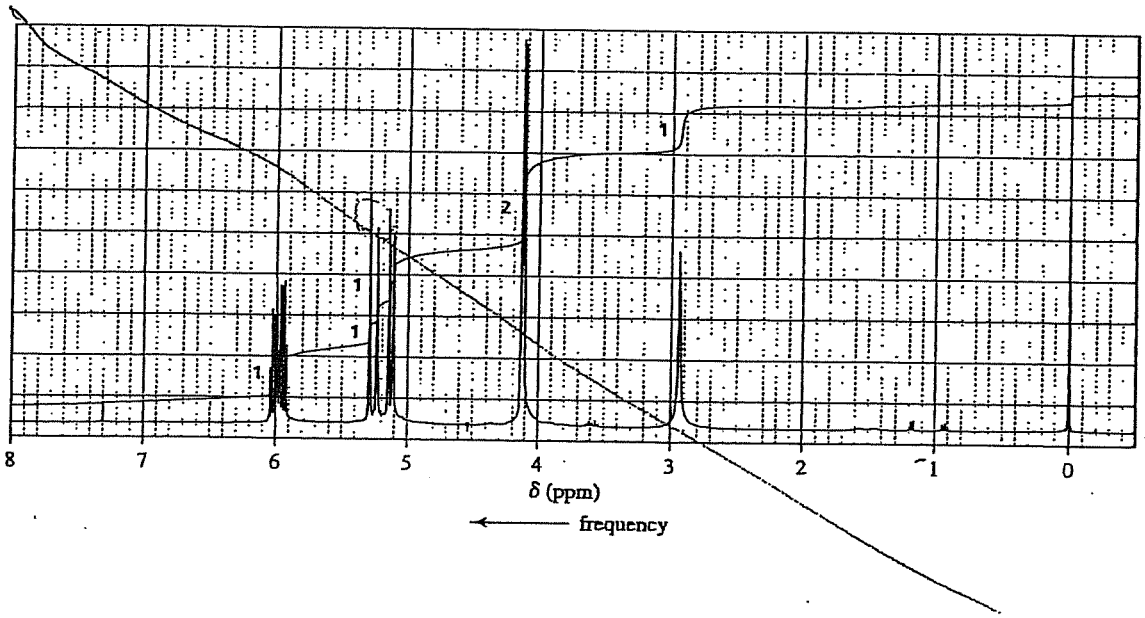
a. $C_4H_{10}O$



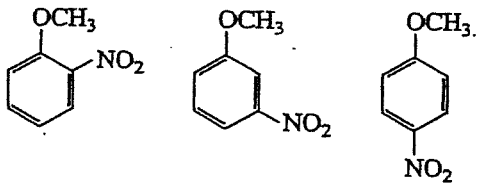
b. $C_6H_{12}O$



0. The ^1H NMR spectrum of 2-propen-1-ol is shown here. Indicate the protons in the molecule that give rise to each of the signals in the spectrum.

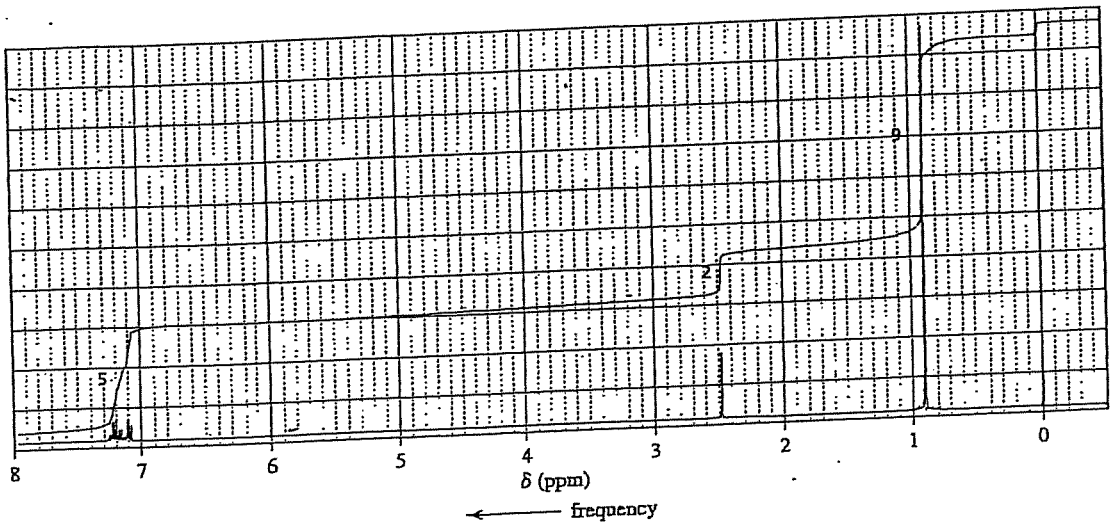


1. How could the signals in the 6.5 to 8.1-ppm region of their ^1H NMR spectra distinguish between the following compounds?

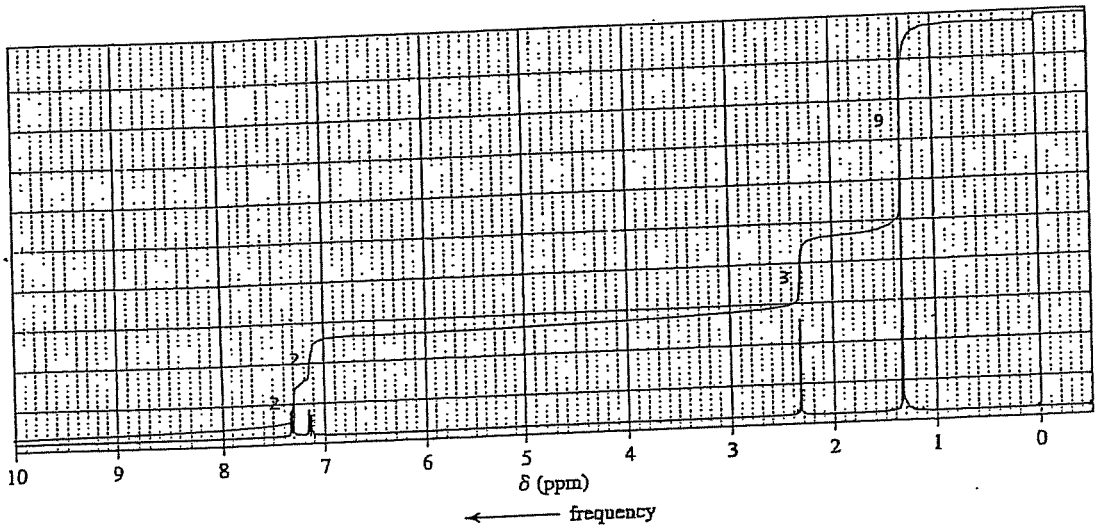


62. The ^{1}H NMR spectra of two compounds, each with molecular formula $C_{11}H_{16}$, are shown here. Identify the compounds.

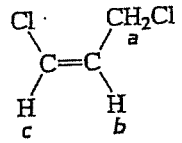
a.



b.



63. Draw a splitting diagram for the H_b proton if $J_{bc} = 10$ and $J_{ba} = 5$.

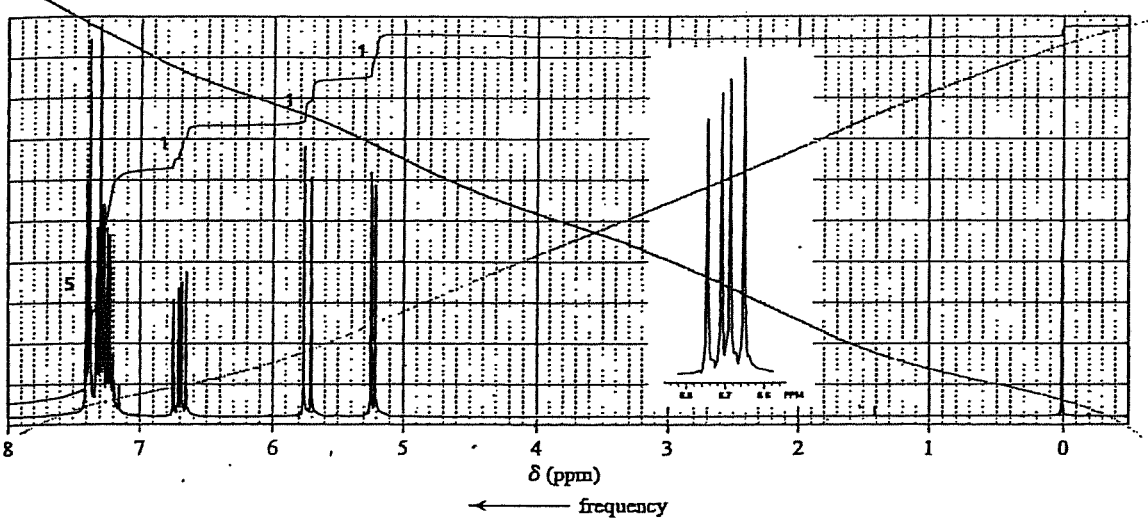


64. Sketch the following spectra that would be obtained for 2-chloroethanol:
   a. the ^{1}H NMR spectrum for a dry sample of the alcohol.
   b. the ^{1}H NMR spectrum for a sample of the alcohol that contains a trace amount of acid.
   c. the ^{13}C NMR spectrum.
   d. the proton-coupled ^{13}C NMR spectrum.
   e. the four parts of a DEPT ^{13}C NMR spectrum.

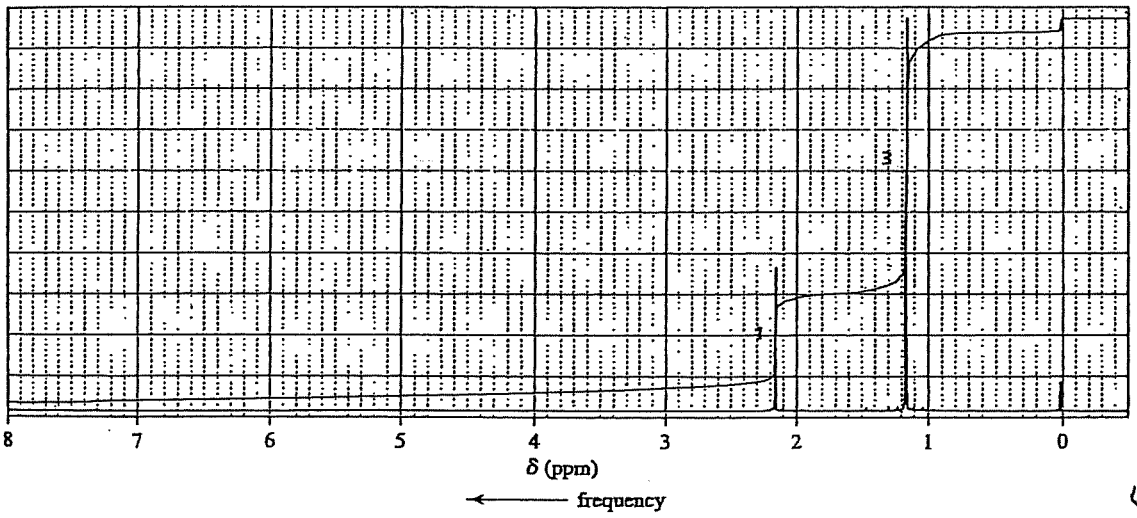
65. How could ^{1}H NMR be used to prove that the addition of HBr to propene follows the rule that says that the electrophile adds to the sp^2 carbon bonded to the greater number of hydrogens?

6. Identify each of the following compounds from its molecular formula and its ^{1}H NMR spectrum.

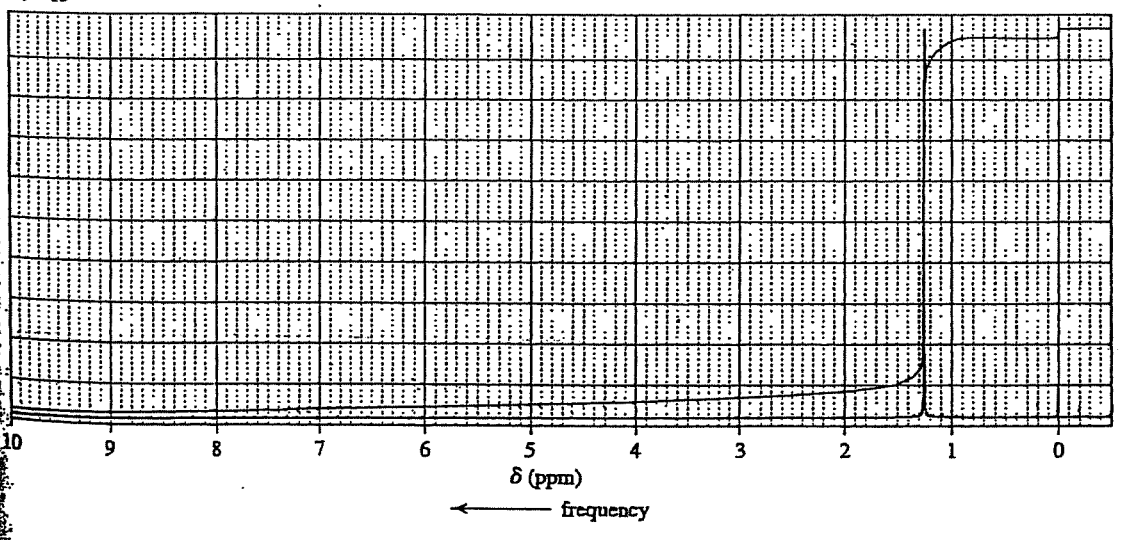
a. C_8H_8



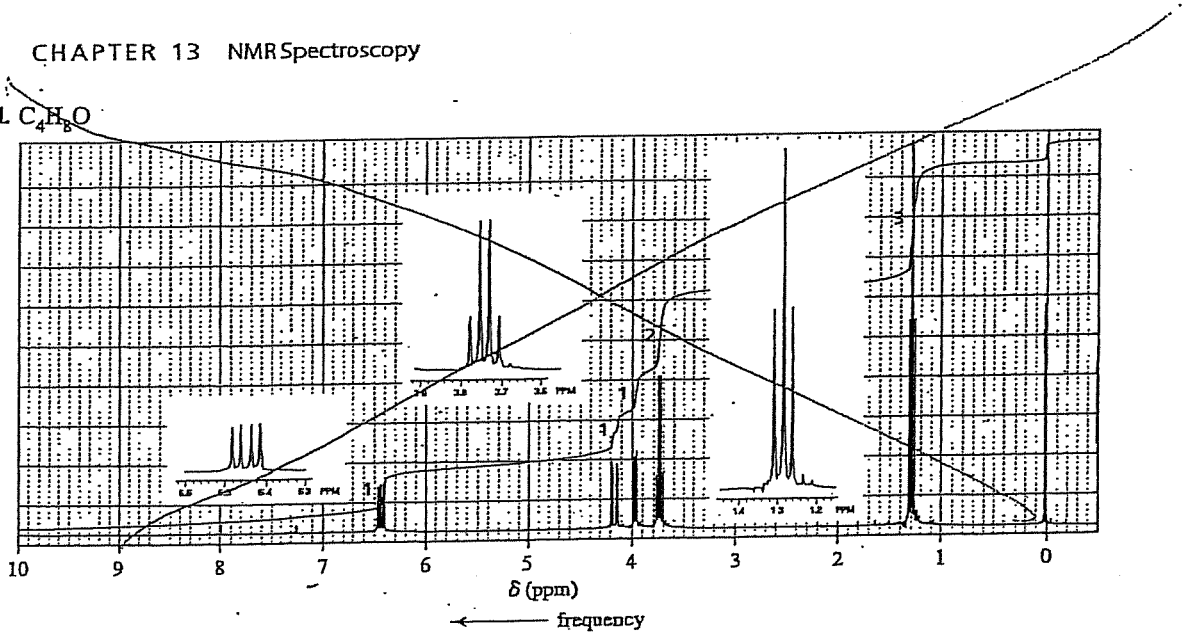
b. $C_6H_{12}O$



c. $C_9H_{18}O$



d. C_4H_8O

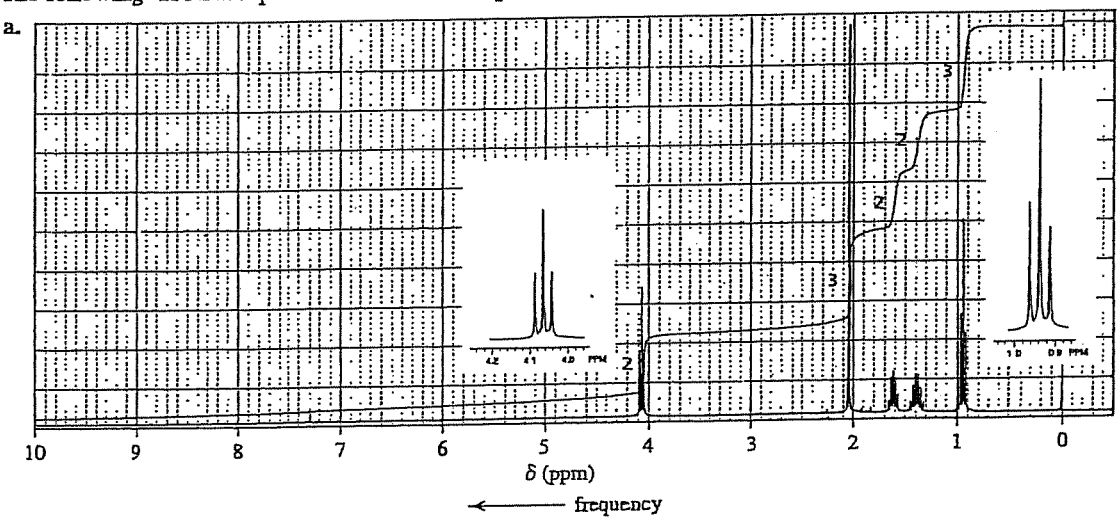


67. Dr. N. M. Arr was called in to help analyze the ^{1}H NMR spectrum of a mixture of compounds known to contain only C, H, and Br. The mixture showed two singlets—one at 1.8 ppm and the other at 2.7 ppm—with relative integrals of 1 : 6, respectively. Dr. Arr determined that the spectrum was that of a mixture of bromomethane and 2-bromo-2-methylpropane. What was the ratio of bromomethane to 2-bromo-2-methylpropane in the mixture?

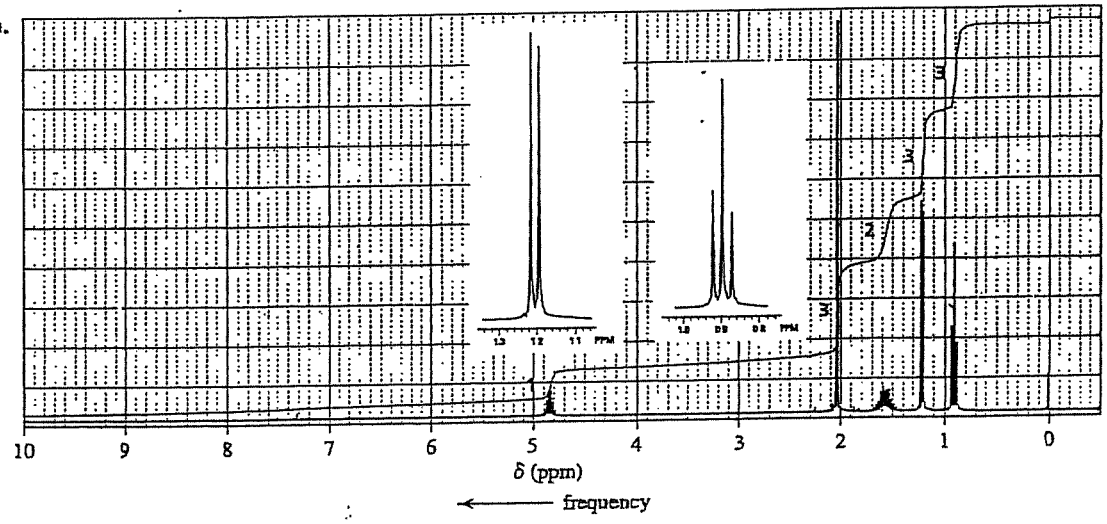
68. Calculate the amount of energy (in calories) required to flip an ^{1}H nucleus in an NMR spectrometer that operates at 60 MHz.

69. The following ^{1}H NMR spectra are for four compounds each with molecular formula $C_6H_{12}O_2$. Identify the compounds.

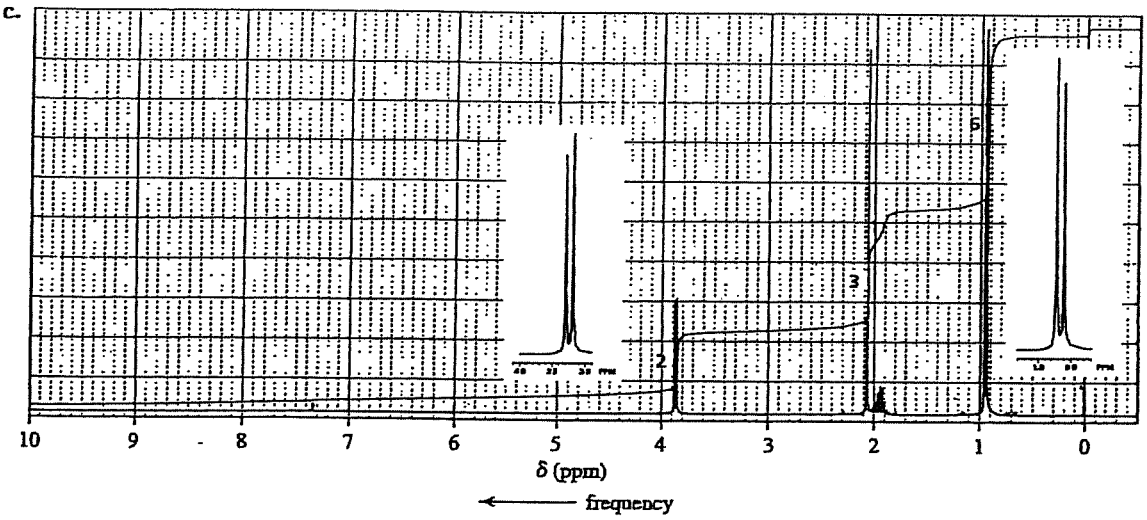
a.



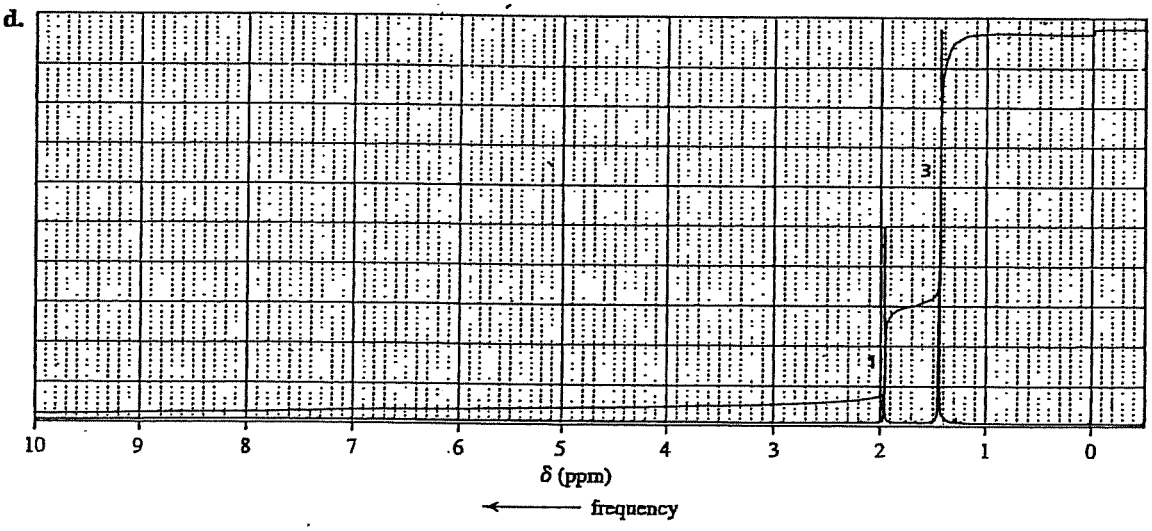
b.



c.



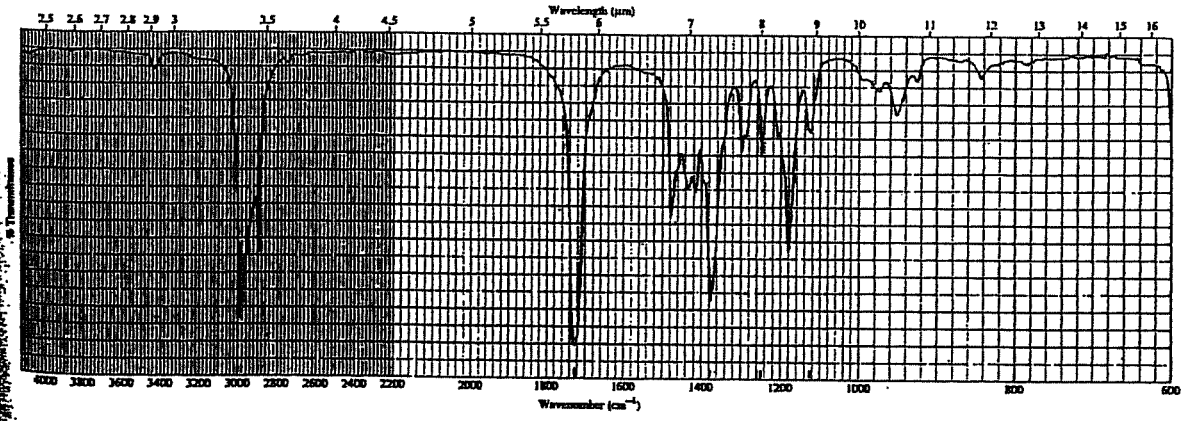
d.

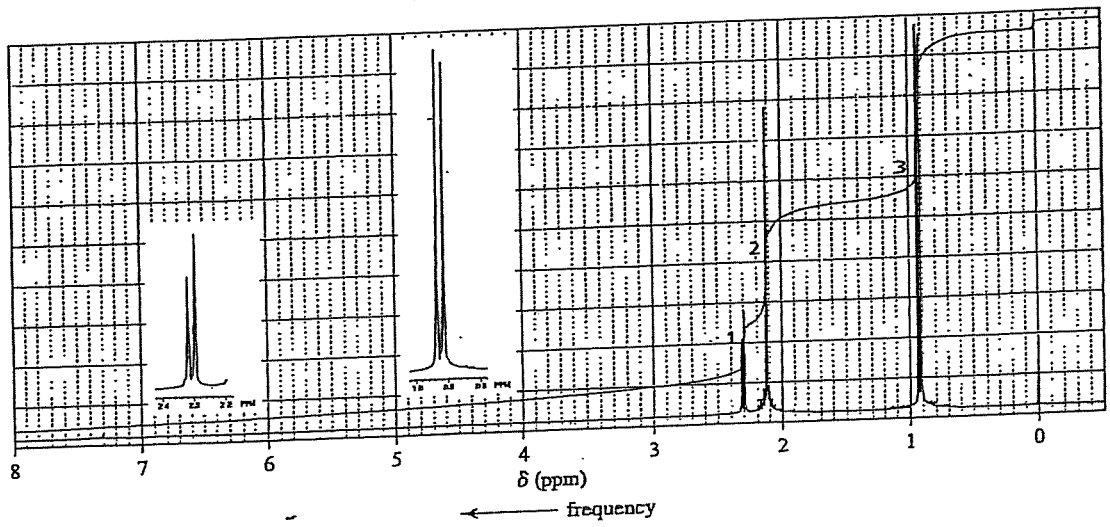


When compound A ($C_5H_{12}O$) is treated with HBr, it forms compound B ($C_5H_{11}Br$). The ^1H NMR spectrum of compound A has one singlet (1), two doublets (3, 6), and two multiplets (both 1). (The relative areas of the signals are indicated in parentheses.) The ^1H NMR spectrum of compound B has a singlet (6), a triplet (3), and a quartet (2). Identify compounds A and B.

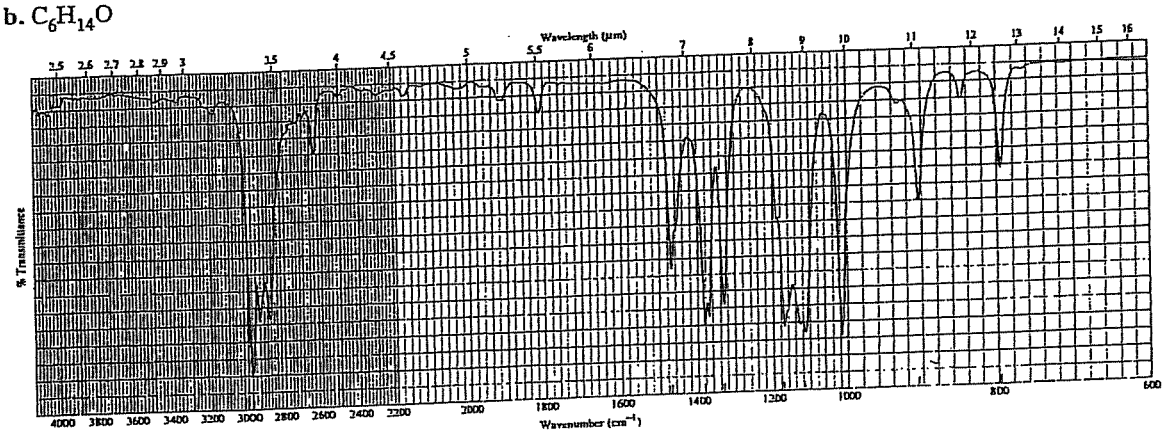
Determine the structure of each of the following compounds, based on its molecular formula and its IR and ^1H NMR spectra.

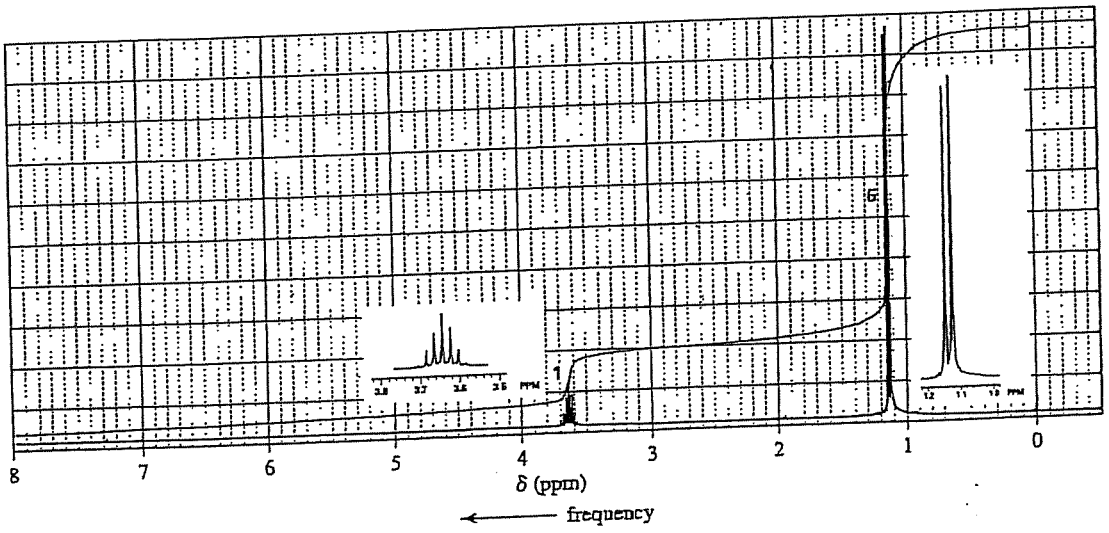
a. $C_6H_{12}O$



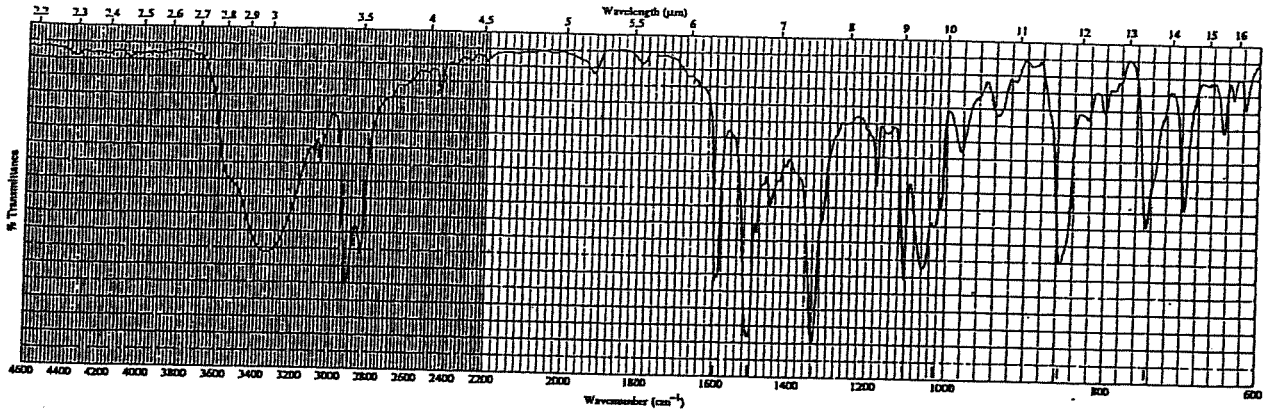

1
2
3
8
7
6
5
4
3
2
1
0
δ (ppm)
frequency

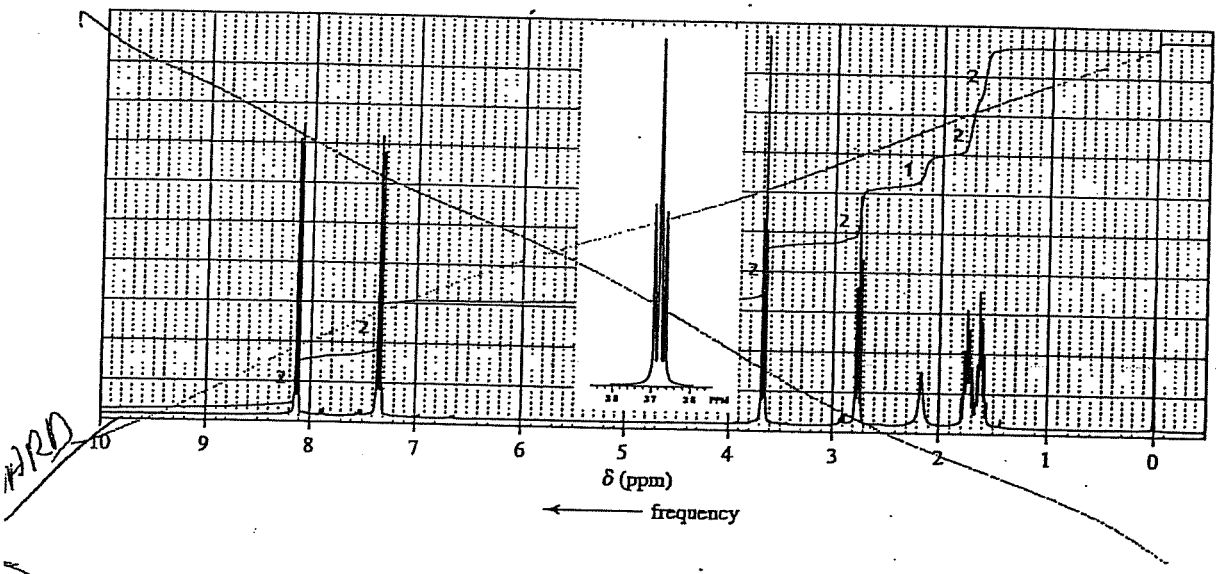
b. $C_6H_{14}O$


Wavelength (μm)
% Transmittance
4000 3800 3600 3400 3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600
Wavenumber (cm⁻¹)

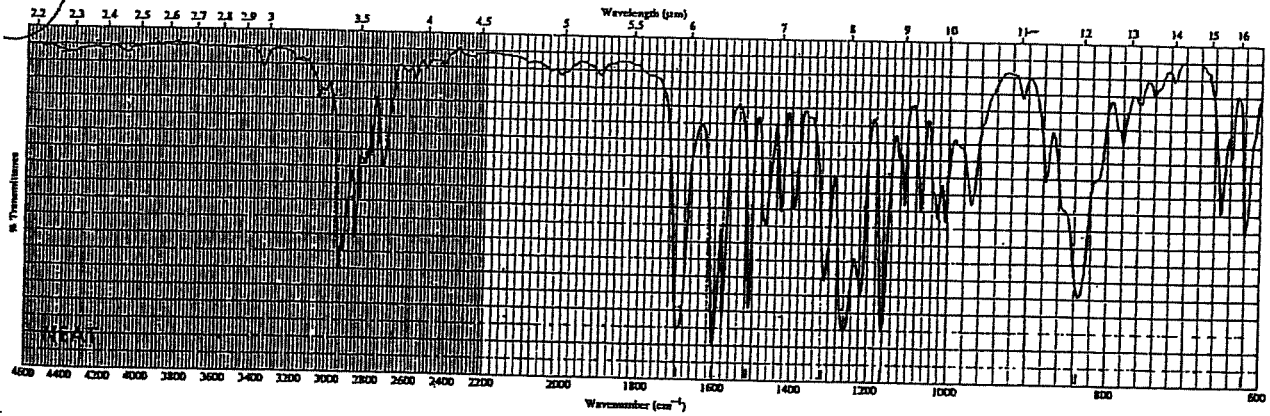

1
6H
8
7
6
5
4
3
2
1
0
δ (ppm)
frequency

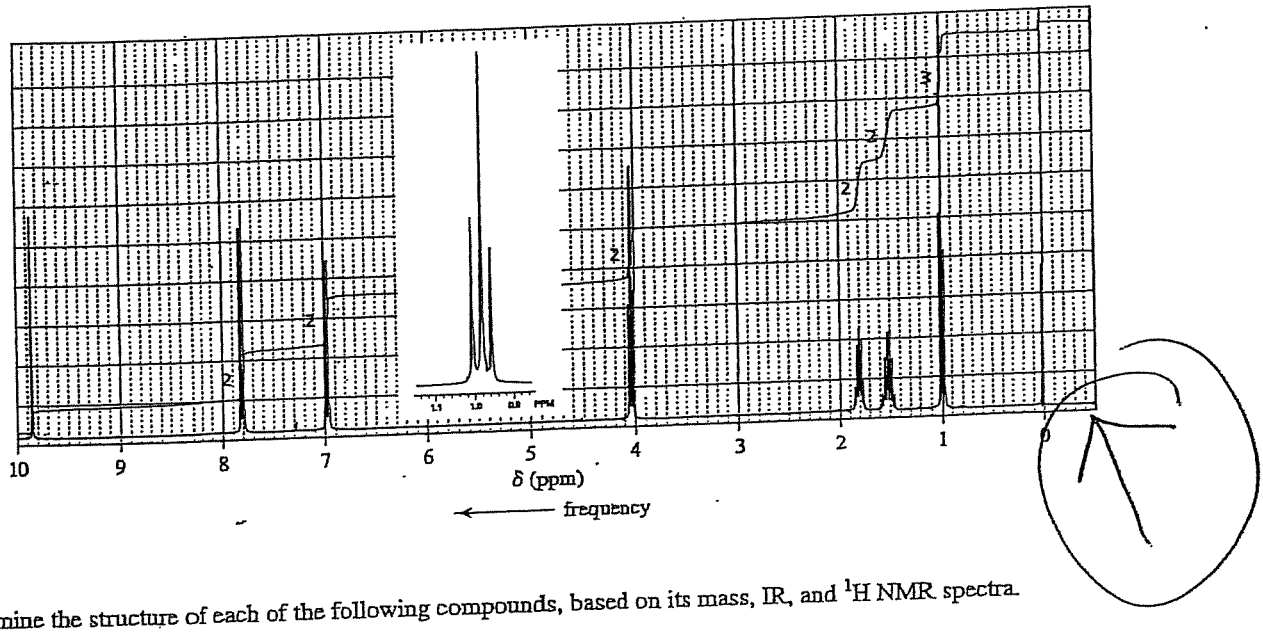
c. $C_{10}H_{13}NO_3$





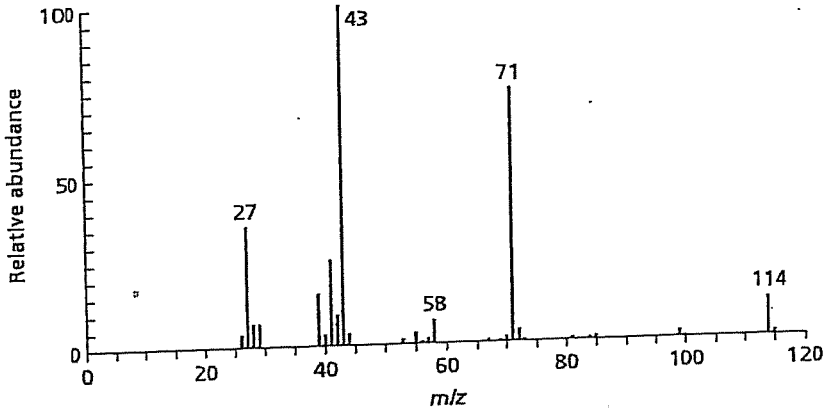
d. $C_{11}H_{14}O_2$

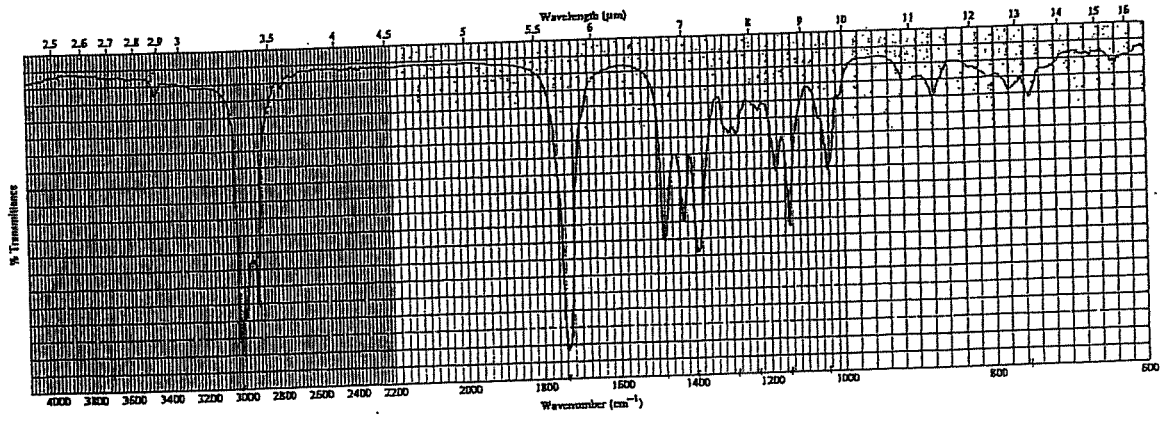


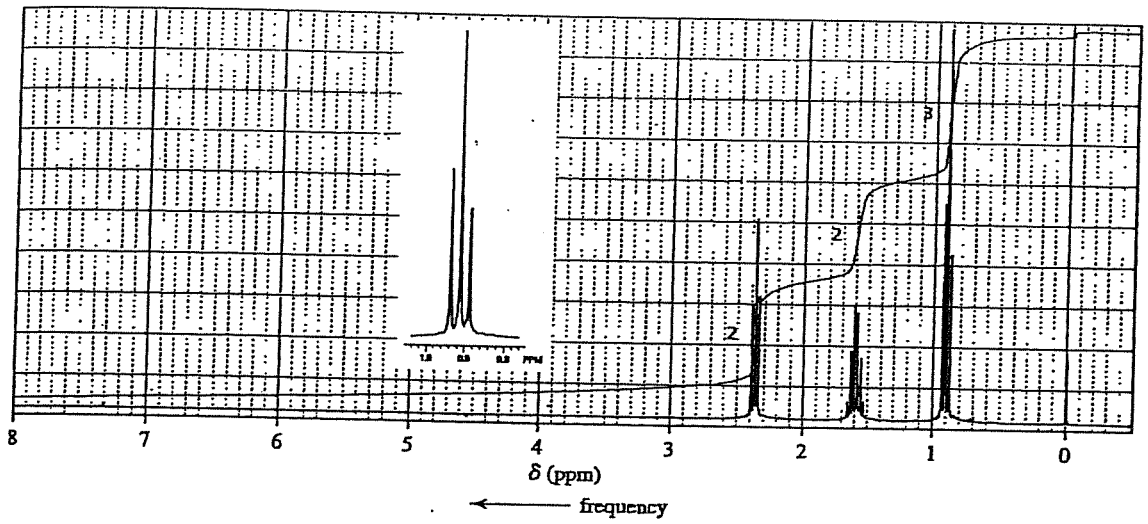


72. Determine the structure of each of the following compounds, based on its mass, IR, and ^{1}H NMR spectra.

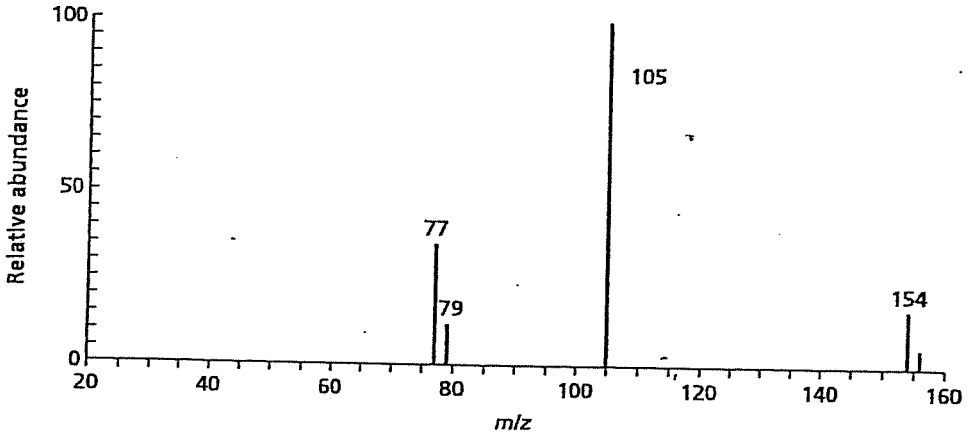
a.

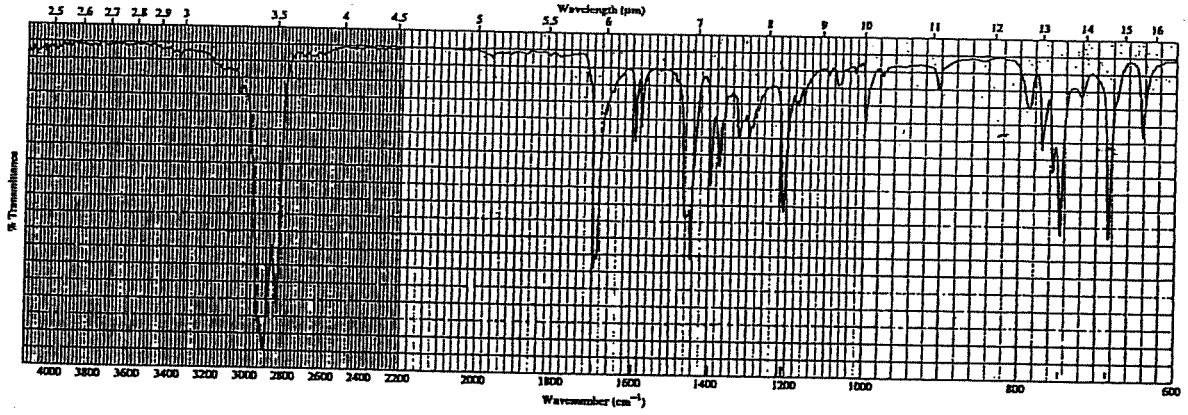


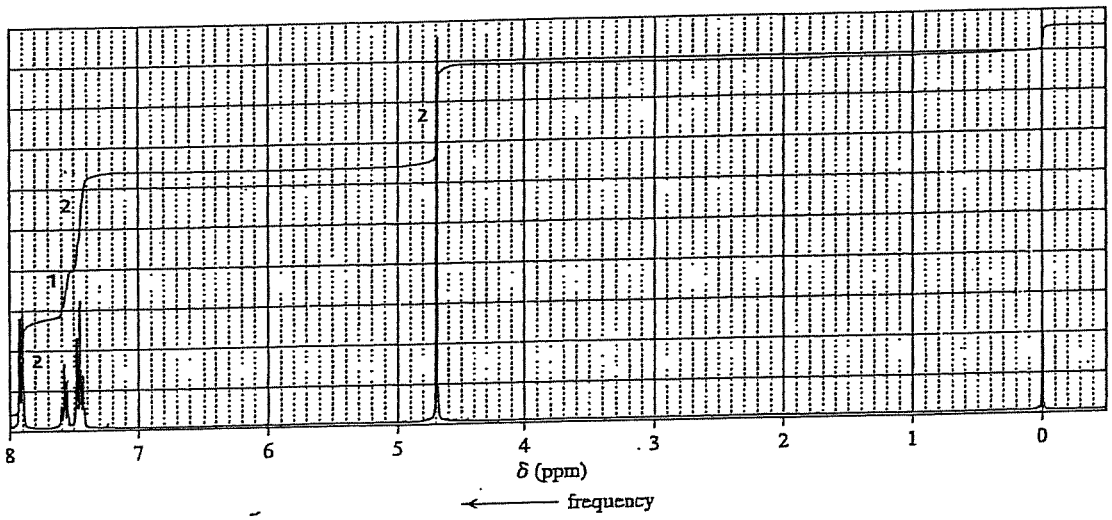



3
2
2
8
7
6
5
4
3
2
1
0
δ (ppm)
frequency

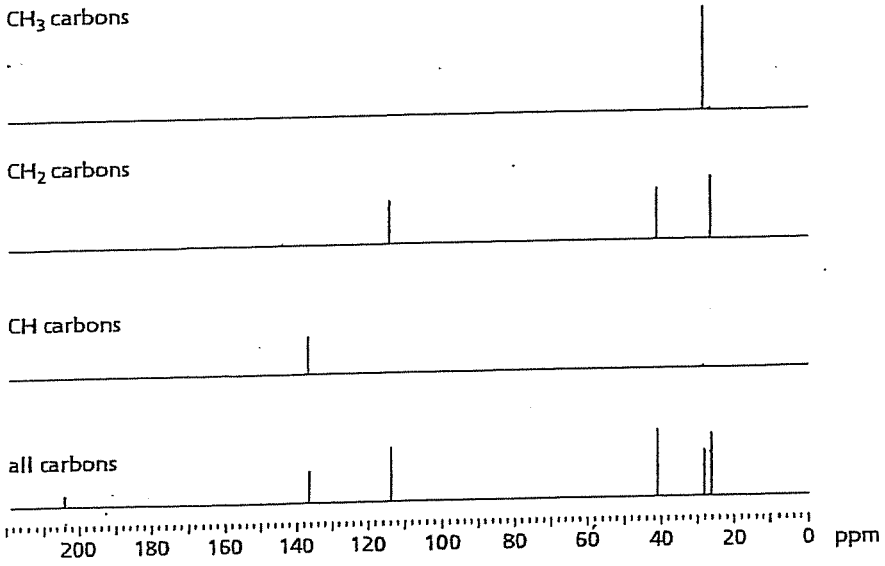
b.


100
50
0
Relative abundance
105
77
79
154
20
40
60
80
100
120
140
160
m/z

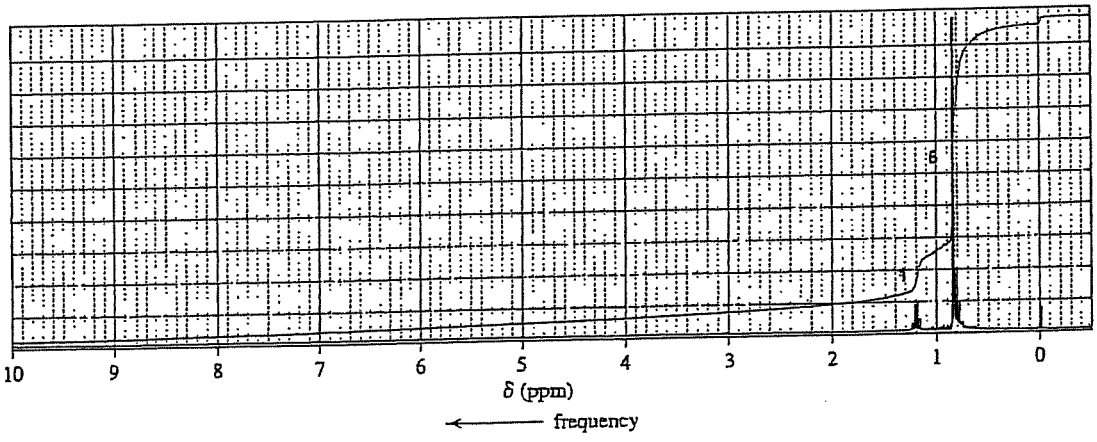

Wavelength (μm)
% Transmittance
Wavenumber (cm⁻¹)

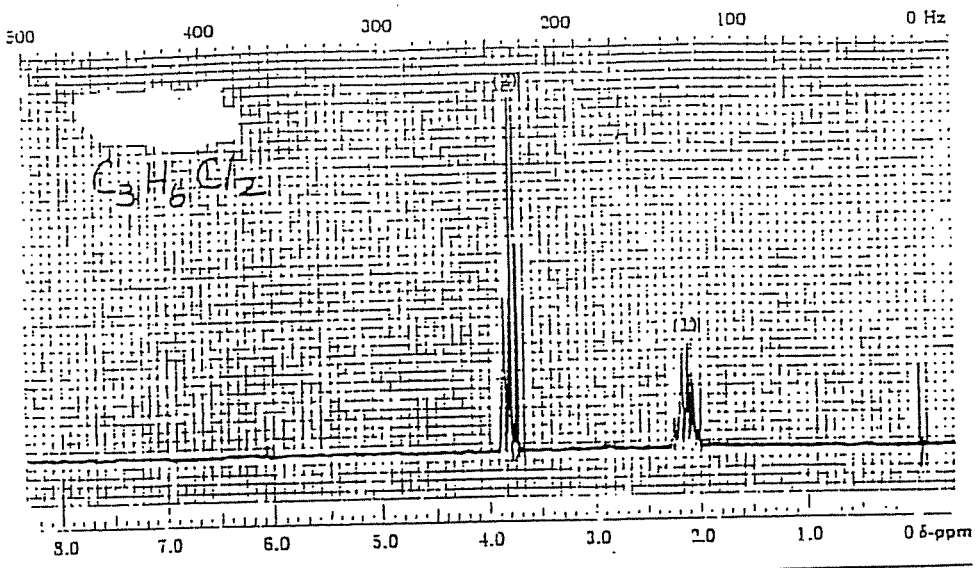


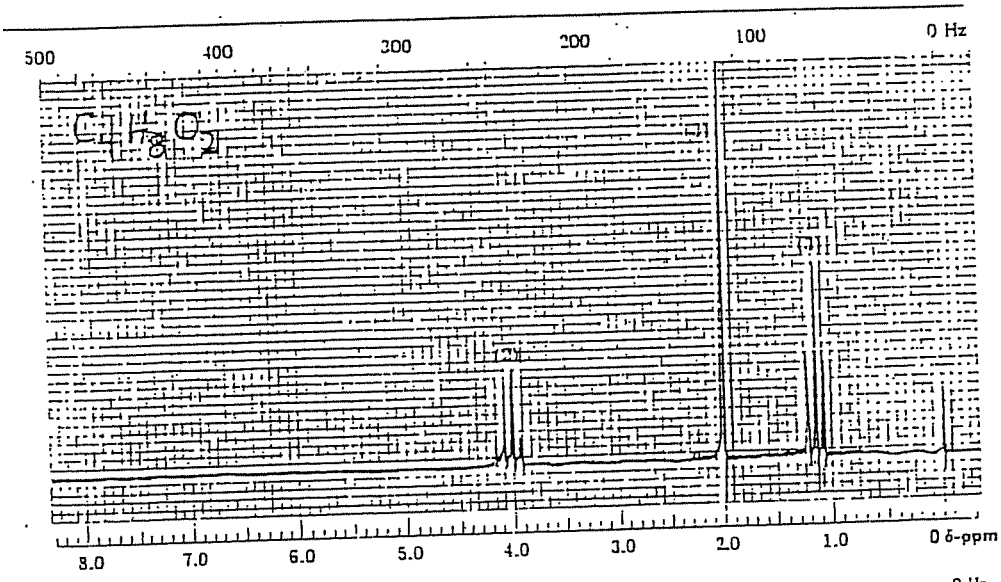
73. Identify the compound with molecular formula $C_6H_{10}O$ that is responsible for the following DEPT ^{13}C NMR spectrum:

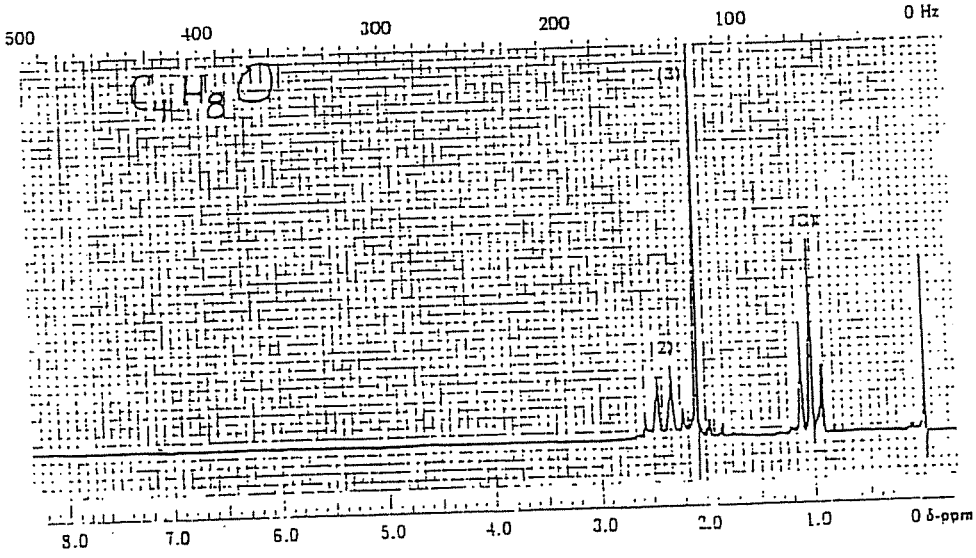


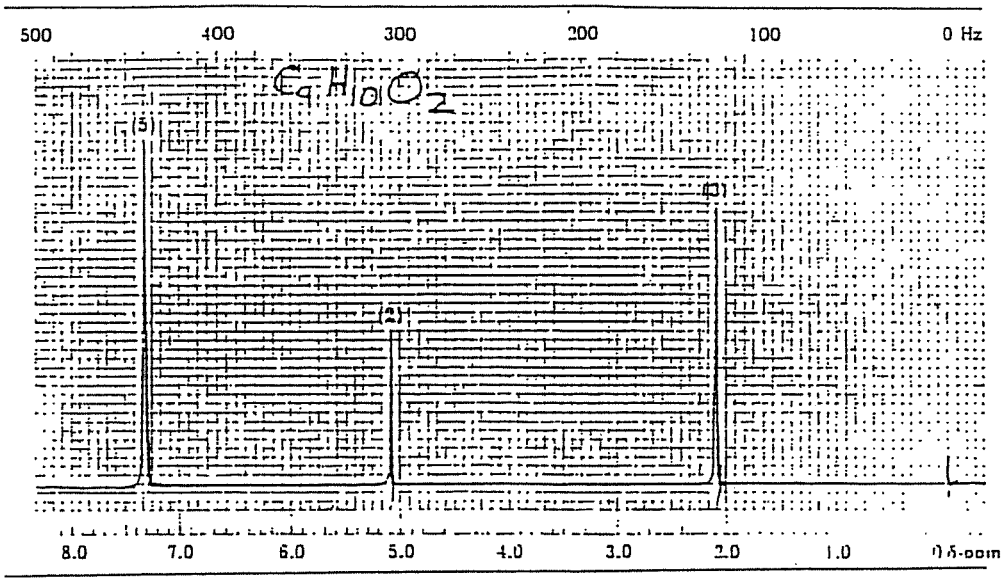
74. Identify the compound with molecular formula C_6H_{14} that is responsible for the following ^1H NMR spectrum:

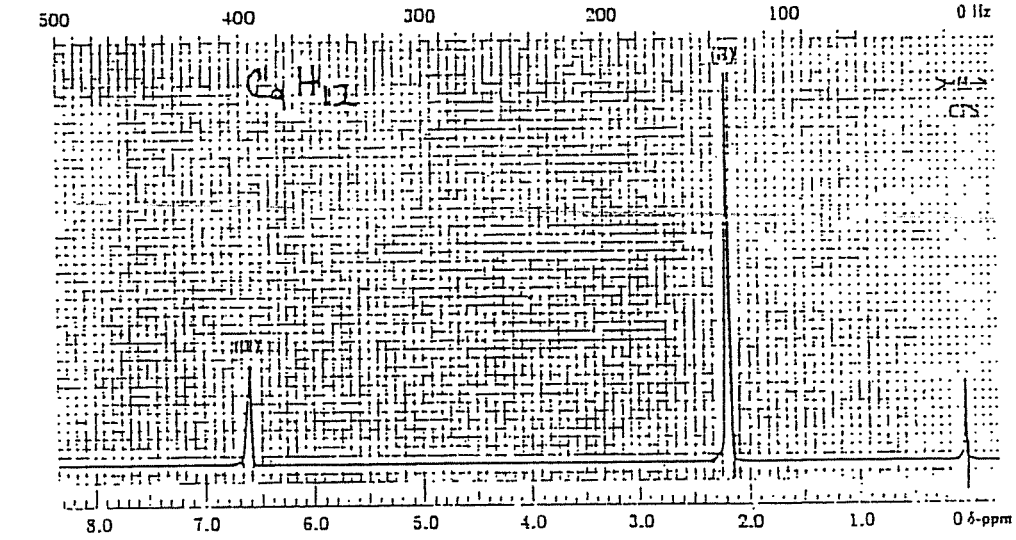


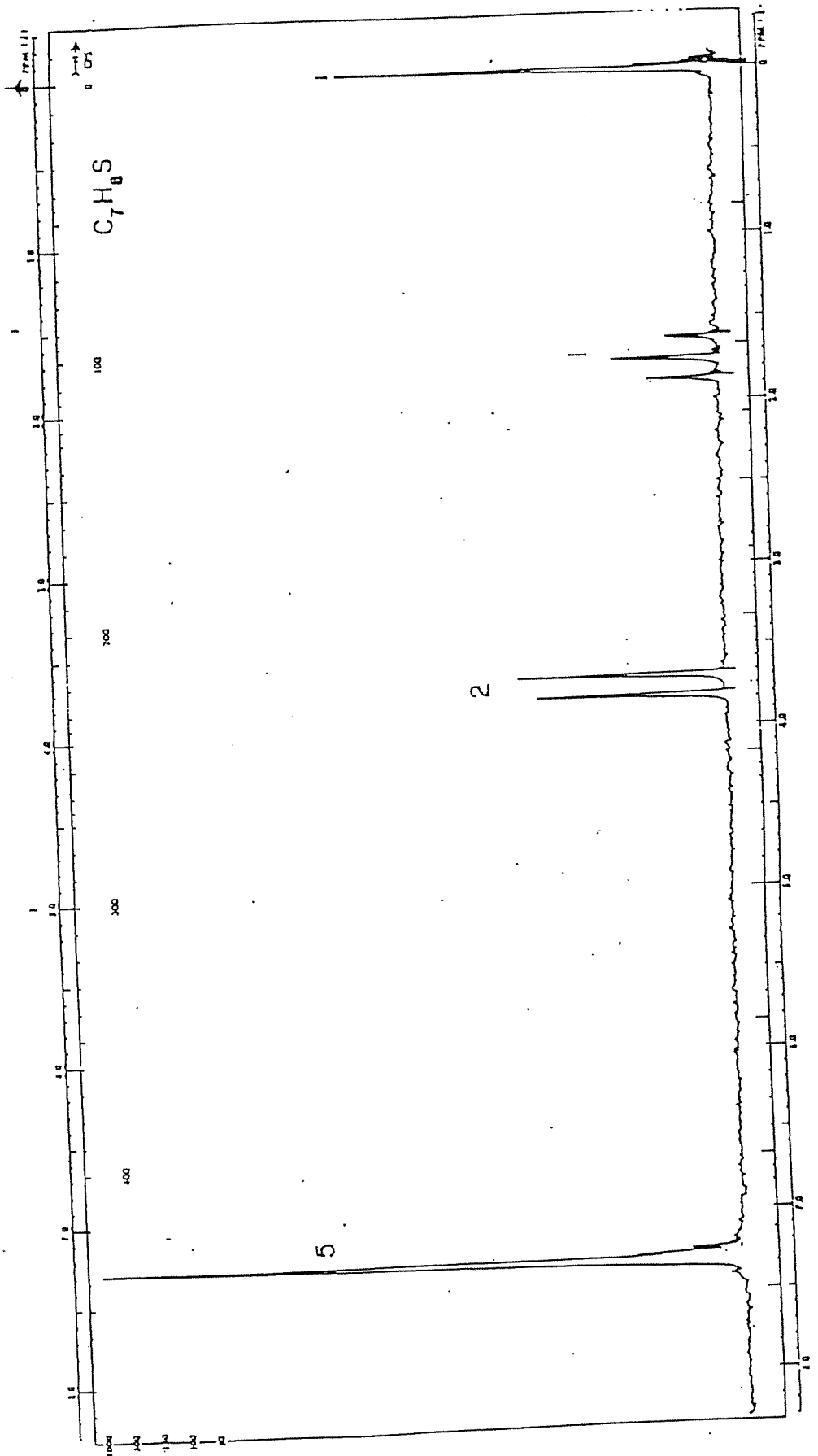

500
400
300
200
100
0 Hz
C3H6Cl2
(2)
(3)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0 δ-ppm


500
400
300
200
100
0 Hz
C4H8O2
(2)
(3)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0 δ-ppm


500
400
300
200
100
0 Hz
C4H8O
(3)
(2)
(1)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0 δ-ppm

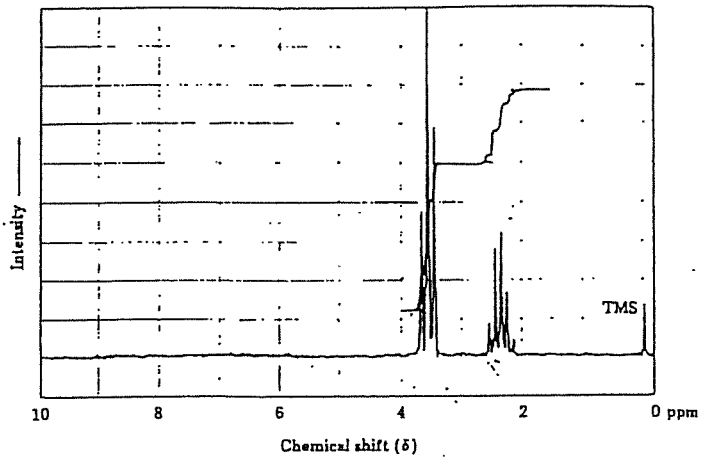

500
400
300
200
100
0 Hz
$C_9H_{10}O_2$
(5)
(1)
(2)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0 δ-ppm


500
400
300
200
100
0 Hz
C_9H_{12}
(3)
CPS
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0 δ-ppm


C_7H_8S
1
2
5

13.39 How could you use IR spectroscopy to help you distinguish between the two compounds shown in Problem 13.38?

13.40 The compound whose ^1H NMR spectrum is shown here has the molecular formula $C_3H_6Br_2$. Propose a plausible structure.

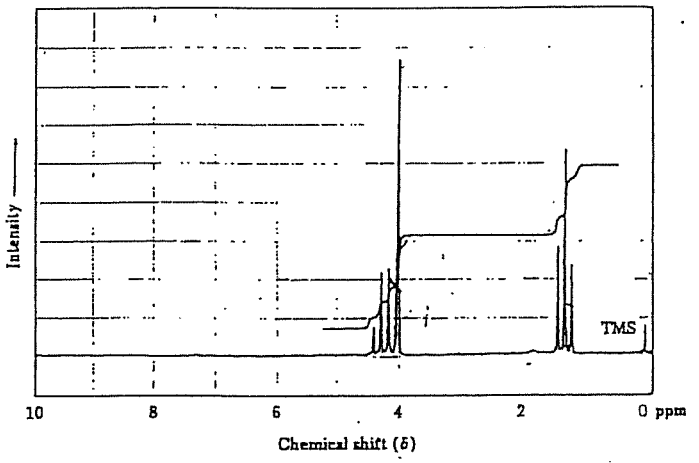


13.41 Propose structures for compounds that fit the following ^1H NMR data:

(a) $C_6H_{10}O$
- 6 H doublet at 0.95 δ, J = 7 Hz
- 3 H singlet at 2.10 δ
- 1 H multiplet at 2.43 δ

(b) C_3H_5Br
- 3 H singlet at 2.32 δ
- 1 H broad singlet at 5.35 δ
- 1 H broad singlet at 5.54 δ

13.42 The compound whose ^1H NMR spectrum is shown has the molecular formula $C_4H_7O_2Cl$ and shows an infrared absorption peak at 1740 cm^{-1}. Propose a plausible structure.



13.43 Propose structures for compounds that fit the following ^1H NMR data:

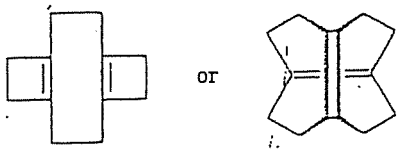
(a) $C_4H_6Cl_2$
- 3 H singlet at 2.18 δ
- 2 H doublet at 4.16 δ, J = 7 Hz
- 1 H triplet at 5.71 δ, J = 7 Hz

(b) $C_{10}H_{14}$
- 9 H singlet at 1.30 δ
- 5 H singlet at 7.30 δ

(c) C_4H_7BrO
3 H singlet at 2.11 δ
2 H triplet at 3.52 δ, J = 6 Hz
2 H triplet at 4.40 δ, J = 6 Hz

(d) $C_9H_{11}Br$
2 H quintet at 2.15 δ, J = 7 Hz
2 H triplet at 2.75 δ, J = 7 Hz
2 H triplet at 3.38 δ, J = 7 Hz
5 H singlet at 7.22 δ

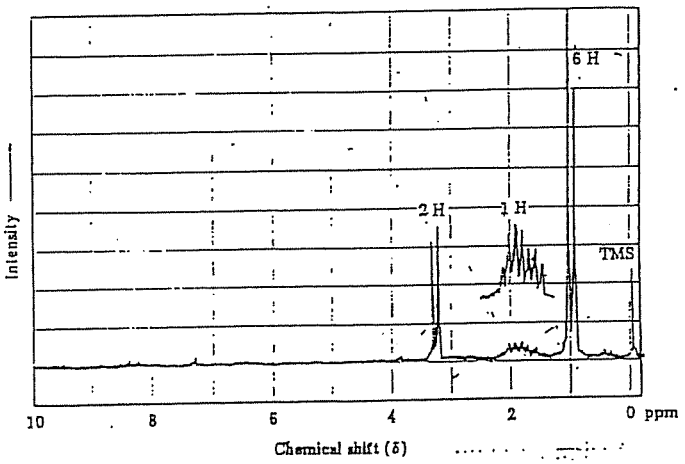
13.44 How might you use NMR (either ^1H or ^{13}C) to differentiate between the following two isomeric structures?



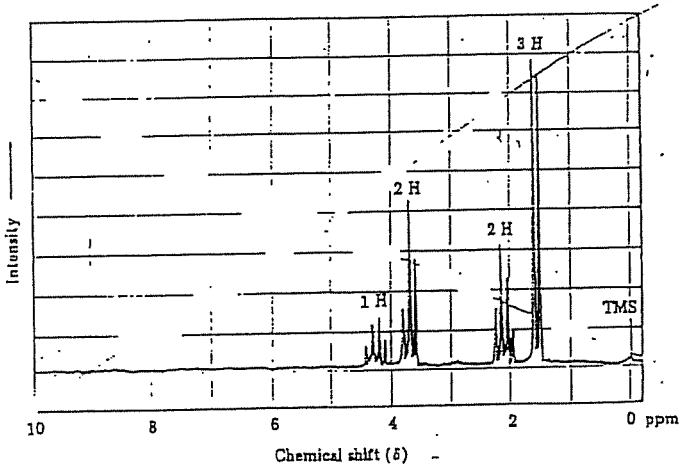
(You might want to build molecular models to help you examine the two structures more closely.)

13.45 Propose plausible structures for the two compounds whose ^1H NMR spectra are shown.

(a) C_4H_9Br

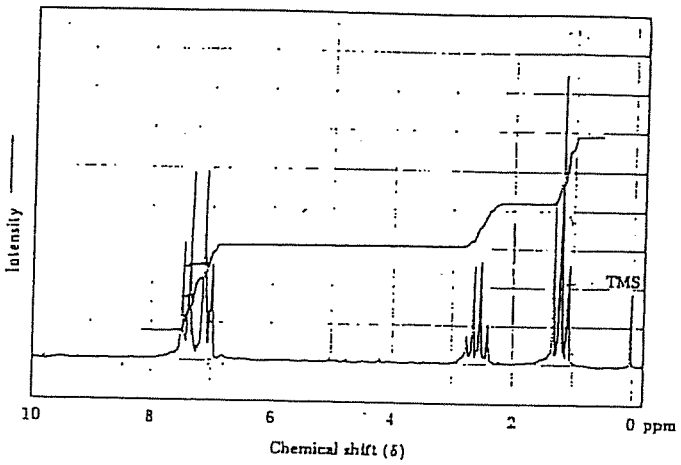


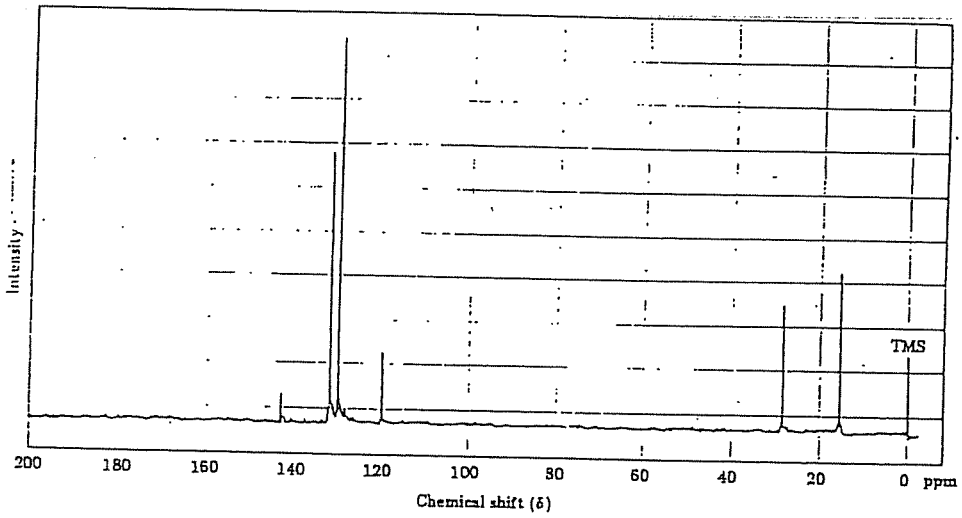
(b) $C_4H_8Cl_2$



13.46 We saw earlier that long-range coupling between protons more than two carbon atoms apart is sometimes observed when pi bonds intervene. One example of long-

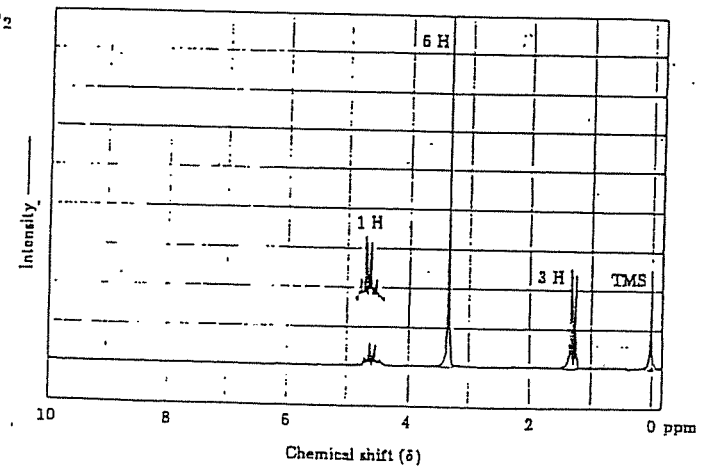
13.48 The ^1H and ^{13}C NMR spectra of compound A, C_8H_9Br, are shown. Propose a possible structure for A, and assign peaks in the spectra to your structure.



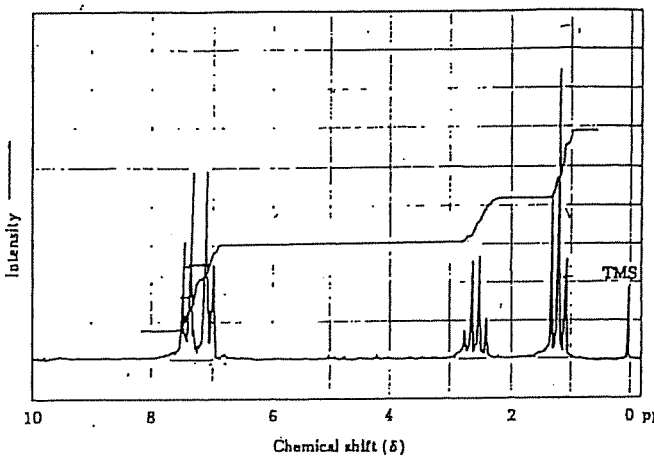


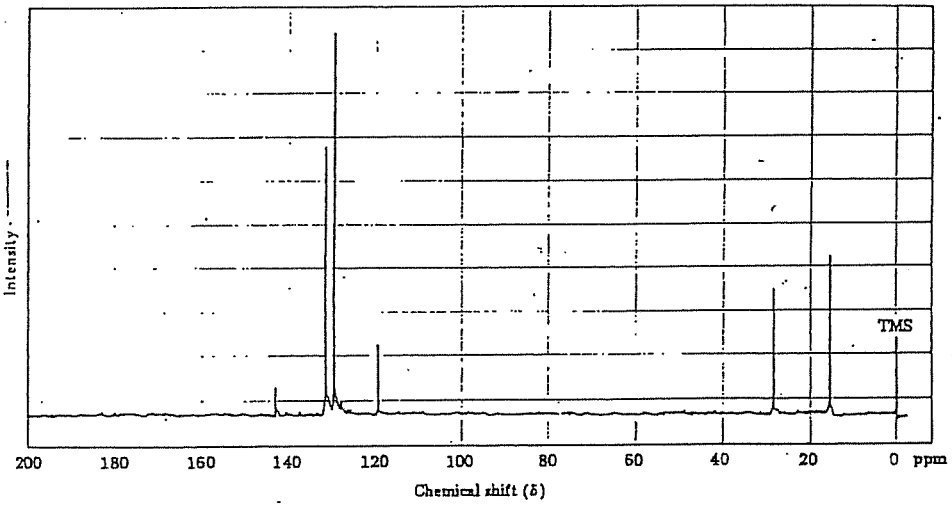
13.49 Propose plausible structures for the three compounds whose ^1H NMR spectra are shown.

(a) $C_4H_{10}O_2$



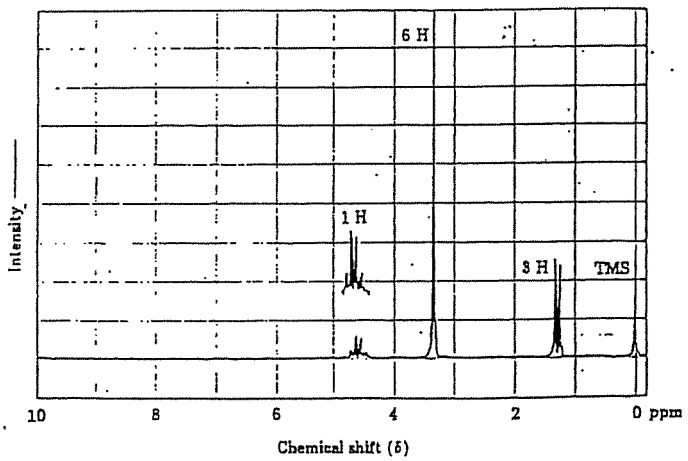
13.48 The ^1H and ^{13}C NMR spectra of compound A, C_8H_9Br, are shown. Propose a possible structure for A, and assign peaks in the spectra to your structure.





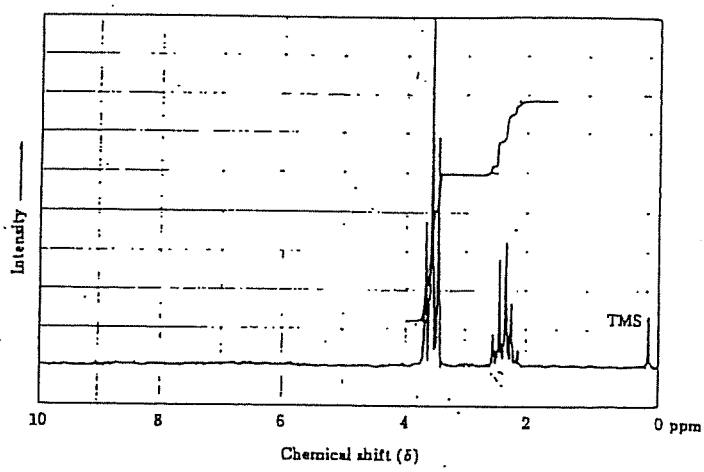
13.49 Propose plausible structures for the three compounds whose ^1H NMR spectra are shown.

(a) $C_4H_{10}O_2$



13.39 How could you use IR spectroscopy to help you distinguish between the two compounds shown in Problem 13.38?

13.40 The compound whose ^1H NMR spectrum is shown here has the molecular formula $C_3H_6Br_2$. Propose a plausible structure.



13.41 Propose structures for compounds that fit the following ^1H NMR data:

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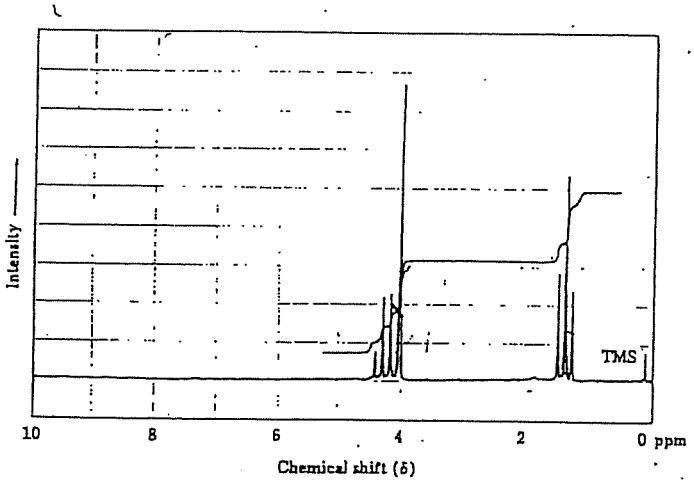
3 H singlet at 2.10 δ
1 H multiplet at 2.43 δ

(b) C_3H_5Br
3 H singlet at 2.32 δ
1 H broad singlet at 5.35 δ
1 H broad singlet at 5.54 δ

13.42 The compound whose ^1H NMR spectrum is shown has the molecular formula $C_4H_7O_2Cl$ and shows an infrared absorption peak at 1740 cm^{-1}. Propose a plausible structure.



13.43 Propose structures for compounds that fit the following ^1H NMR data:

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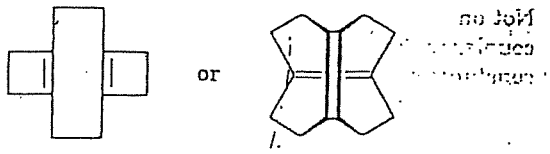
3 H singlet at 2.18 δ
2 H doublet at 4.16 δ, J = 7 Hz
1 H triplet at 5.71 δ, J = 7 Hz

(b) $C_{10}H_{14}$
9 H singlet at 1.30 δ
5 H singlet at 7.30 δ

(c) C_4H_7BrO
3 H singlet at 2.11 δ
2 H triplet at 3.52 δ, J = 6 Hz
2 H triplet at 4.40 δ, J = 6 Hz

(d) $C_9H_{11}Br$
2 H quintet at 2.15 δ, J = 7 Hz
2 H triplet at 2.75 δ, J = 7 Hz
2 H triplet at 3.38 δ, J = 7 Hz
5 H singlet at 7.22 δ

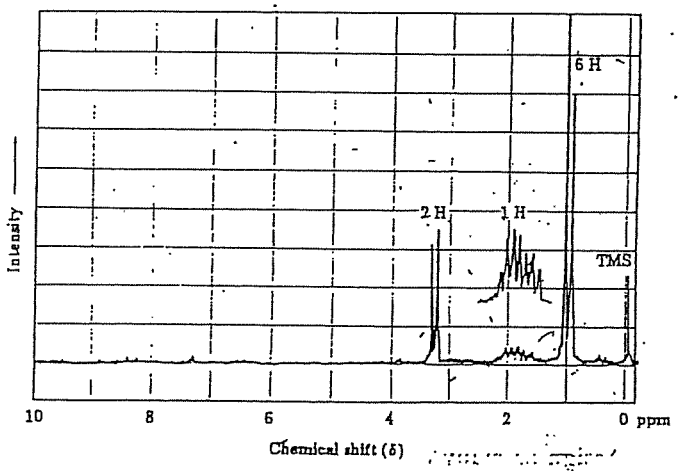
13.44 How might you use NMR (either ^1H or ^{13}C) to differentiate between the following two isomeric structures?



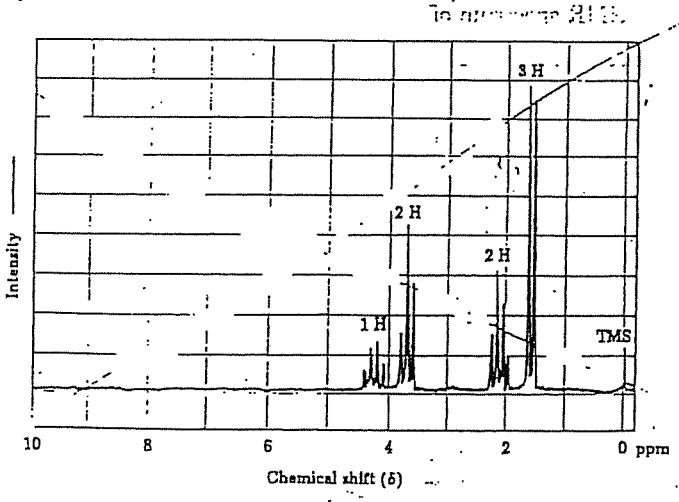
(You might want to build molecular models to help you examine the two structures more closely.)

13.45 Propose plausible structures for the two compounds whose ^1H NMR spectra are shown.

(a) C_4H_9Br



(b) $C_4H_8Cl_2$



13.46 We saw earlier that long-range coupling between protons more than two carbon atoms apart is sometimes observed when pi bonds intervene. One example of long-

S_N2 vs. E_2 vs. S_N1 vs. E_1

Back to Web Book **See entire flow chart**

Does substrate have good leaving group?

No
No Rxn

Yes
Is the nucleophile/base strong?

No
Nature of Substrate

1º	**2º**	**3º**
No Rxn	S_N1/E_1	S_N1/E_1

Yes
Nuclophile or base?

Nucleophile
Nature of substrate?

1º	**2º**	**3º**
S_N2	S_N2/S_N1 *Nature of solvent?*	S_N1

polar protic	**polar, aprotic**
S_N1 favored	S_N2 favored

base
Nature of substrate?

1º	**2º**	**3º**
S_N2	*Is base bulky?*	E_2

Yes	**No**
E_2	S_N2/E_2

WebElements: the periodic table on the world-wide web

www.webelements.com

1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
hydrogen 1 **H** 1.0079																		helium 2 **He** 4.0026
lithium 3 **Li** 6.941	beryllium 4 **Be** 9.0122												boron 5 **B** 10.811	carbon 6 **C** 12.011	nitrogen 7 **N** 14.007	oxygen 8 **O** 15.999	fluorine 9 **F** 18.998	neon 10 **Ne** 20.180
sodium 11 **Na** 22.990	magnesium 12 **Mg** 24.305												aluminium 13 **Al** 26.982	silicon 14 **Si** 28.086	phosphorus 15 **P** 30.974	sulfur 16 **S** 32.065	chlorine 17 **Cl** 35.453	argon 18 **Ar** 39.948
potassium 19 **K** 39.098	calcium 20 **Ca** 40.078		scandium 21 **Sc** 44.956	titanium 22 **Ti** 47.867	vanadium 23 **V** 50.942	chromium 24 **Cr** 51.996	manganese 25 **Mn** 54.938	iron 26 **Fe** 55.845	cobalt 27 **Co** 58.933	nickel 28 **Ni** 58.693	copper 29 **Cu** 63.546	zinc 30 **Zn** 65.38	gallium 31 **Ga** 69.723	germanium 32 **Ge** 72.61	arsenic 33 **As** 74.922	selenium 34 **Se** 78.96	bromine 35 **Br** 79.904	krypton 36 **Kr** 83.80
rubidium 37 **Rb** 85.468	strontium 38 **Sr** 87.62		yttrium 39 **Y** 88.906	zirconium 40 **Zr** 91.224	niobium 41 **Nb** 92.906	molybdenum 42 **Mo** 95.96	technetium 43 **Tc** [98]	ruthenium 44 **Ru** 101.07	rhodium 45 **Rh** 102.91	palladium 46 **Pd** 106.42	silver 47 **Ag** 107.87	cadmium 48 **Cd** 112.41	indium 49 **In** 114.82	tin 50 **Sn** 118.71	antimony 51 **Sb** 121.76	tellurium 52 **Te** 127.60	iodine 53 **I** 126.90	xenon 54 **Xe** 131.29
caesium 55 **Cs** 132.91	barium 56 **Ba** 137.33	57-70 *	lutetium 71 **Lu** 174.97	hafnium 72 **Hf** 178.49	tantalum 73 **Ta** 180.95	tungsten 74 **W** 183.84	rhenium 75 **Re** 186.21	osmium 76 **Os** 190.23	iridium 77 **Ir** 192.22	platinum 78 **Pt** 195.08	gold 79 **Au** 196.97	mercury 80 **Hg** 200.59	thallium 81 **Tl** 204.38	lead 82 **Pb** 207.2	bismuth 83 **Bi** 208.98	polonium 84 **Po** [209]	astatine 85 **At** [210]	radon 86 **Rn** [222]
francium 87 **Fr** [223]	radium 88 **Ra** [226]	89-102 **	lawrencium 103 **Lr** [262]	rutherfordium 104 **Rf** [267]	dubnium 105 **Db** [268]	seaborgium 106 **Sg** [271]	bohrium 107 **Bh** [272]	hassium 108 **Hs** [270]	meitnerium 109 **Mt** [276]	darmstadtium 110 **Ds** [281]	roentgenium 111 **Rg** [280]	ununbium 112 **Uub** [285]	ununtrium 113 **Uut** [284]	ununquadium 114 **Uuq** [289]	ununpentium 115 **Uup** [288]	ununhexium 116 **Uuh** [293]	ununseptium 117 Uus –	ununoctium 118 **Uuo** [294]

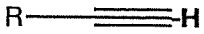
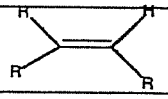
Key:

element name
atomic number
symbol
atomic weight (mean relative mass)

*lanthanoids	lanthanum 57 **La** 138.91	cerium 58 **Ce** 140.12	praseodymium 59 **Pr** 140.91	neodymium 60 **Nd** 144.24	promethium 61 **Pm** [145]	samarium 62 **Sm** 150.36	europium 63 **Eu** 151.96	gadolinium 64 **Gd** 157.25	terbium 65 **Tb** 158.93	dysprosium 66 **Dy** 162.50	holmium 67 **Ho** 164.93	erbium 68 **Er** 167.26	thulium 69 **Tm** 168.93	ytterbium 70 **Yb** 173.06
**actinoids	actinium 89 **Ac** [227]	thorium 90 **Th** 232.04	protactinium 91 **Pa** 231.04	uranium 92 **U** 238.03	neptunium 93 **Np** [237]	plutonium 94 **Pu** [244]	americium 95 **Am** [243]	curium 96 **Cm** [247]	berkelium 97 **Bk** [247]	californium 98 **Cf** [251]	einsteinium 99 **Es** [252]	fermium 100 **Fm** [257]	mendelevium 101 **Md** [256]	nobelium 102 **No** [259]

Symbols and names: the symbols and names of the elements, and their spellings are those recommended by the International Union of Pure and Applied Chemistry (IUPAC - http://www.iupac.org/). Names have yet to be proposed for the most recently discovered elements beyond 112 and so those used here are IUPAC's temporary systematic names. In the USA and some other countries, the spellings aluminum and cesium are normal while in the UK and elsewhere the common spelling is sulphur.
Group labels: the numeric system (1–18) used here is the current IUPAC convention.
Atomic weights (mean relative masses): Apart from the heaviest elements, these are the IUPAC 2007 values and given to 5 significant figures. Elements for which the atomic weight is given within square brackets have no stable nuclides and are represented by the element's longest lived isotope reported at the time of writing.

^{1}H NMR CHEMICAL SHIFT CHART*

Type of Proton	Formula	Chemical Shift
Reference peak	$Si(CH_3)_4$	0
Saturated primary	RCH_3	0.7-1.3
Saturated secondary	RCH_2R	1.2-1.4
Saturated tertiary	$RCHR_2$	1.4-1.7
Allylic primary		1.6-1.9
Methyl ketones	$RCOCH_3$	2.1-2.4
Aromatic methyl	$Ph\text{-}CH_3$	2.5-2.7
Alkyl chloride	$R\text{-}CH_2Cl$	3.0-4.0
Alkyl bromide	$R\text{-}CH_2Br$	2.5-4.0
Alkyl iodide	$R\text{-}CH_2I$	2.5-4.0
alkyl amine	RNH_2	Extremely variable (1-5)
Alcohol, ether	$R\text{-}CH_2O\text{-}R'$	3.3-4.0
Alkynyl		2.5-2.7
Vinylic		5.0-6.5
Aromatic	$Ph\text{-}H$	5.6-8.0
Aldehyde	$RCOH$	9.7-10.0
Carboxylic acid	$RCOOH$	11.0-12.0
Alcohol	ROH	Extremely variable (2.5-5.0)

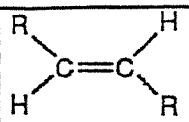
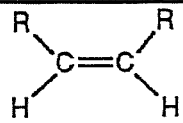
*data from McMurry, J. *Organic Chemistry*, Third edition, Brooks-Cole, California, 1992

please note: Ph = phenyl or an aromatic ring, the CO in the ketone and aldehyde is a carbonyl, ie, C=O

CHARACTERISTIC INFRARED FREQUENCIES*

cm^{-1}	Functional group	Comments
3600-3400	O-H stretching	3600-3500 cm^{-1} (sharp, often weak) from "free" or unassociated O-H; 3400-3200 cm^{-1} (broad) from H-bonded (associated) O-H. Carboxylic acids and β-dicarbonyl compounds have very strongly associated O-H with a very broad absorption (500 cm^{-1}) centered at 3000-2900 cm^{-1}.
3500-3200	N-H stretching	3300 cm^{-1} (sharp) from unassociated N-H; 3200 cm^{-1} (broad) from associated N-H. An NH_2 group usually appears as a doublet (ca. 50 cm^{-1} apart); N-H of a 2° amine often weak.
3300	C-H stretching terminal alkyne	Usually very sharp and strong in RC≡CH; look for confirmatory C≡C stretching at 2260-2100 cm^{-1}. Complete absence of absorption at 3300-3000 cm^{-1} indicates absence of H bonded C=C or C≡C; may be weak in large molecules.
3100-3000	C-H stretching alkene arene cyclopropane	Often weak in alkenes of high molecular weight. Symmetrical stretching of $=CH_2$ (2975 cm^{-1}) overlaps with alkane absorption.
3000-2800	C-H stretching alkane	Usually strong and multi-banded due to symmetrical and asymmetrical stretching as well as methyl, methylene, and methine differences. Absence of absorption indicates lack of sp^3 H-bearing carbon.
2820-2720	C-H stretching aldehyde	Often shows two bands from combination or overtone. Correlate with aldehyde C=O stretching at 1725 cm^{-1}.
2250-2225	C≡N stretching nitrile	2250 cm^{-1} unconjugated nitrile; 2225 cm^{-1} conjugated nitrile (special calibration usually needed to distinguish).
2260-2100	C≡C stretching	Moderate for terminal alkynes; very weak or absent if alkyne is nearly symmetrical.
2260-2100	C≡X=Y stretching	C=C=O stretching of ketenes (2150 cm^{-1}) and N=C=O stretching of isocyanates (2250 cm^{-1}) are very strong and characteristic.
1950	C=C=C stretching allene	Intensity depends on polarity of substituents. Other bands in the 2500-1900 cm^{-1} region can arise from S-H stretching (2600-2550 cm^{-1}, weak) and P-H stretching (2440-2350 cm^{-1}, medium) besides various overtone and combination absorptions.
1820 and 1760	C=O stretching of acid anhydride	Both bands are present and are altered by conjugation and ring size if cyclic. The bands are also present, but closer together, in diacyl perioxides.
1800	C=O stretching acyl chloride	Lowered to 1780-1760 cm^{-1} by conjugation.

cm^{-1}	Functional group	Comments
1770	C=O stretching γ-lactone	Lowered to ca. 1750 cm^{-1} by conjugation.
1745	C=O stretching 5-membered cyclic ketone	Lowered to ca. 1715 cm^{-1} by conjugation.
1735	C=O stretching ester	Lowered to ca. 1710 cm^{-1} by conjugation. Raised to ca. 1760 cm^{-1} by vinyl attached to oxygen.
1725	C=O stretching aldehyde	Lowered to ca. 1690 cm^{-1} by conjugation.
1715	C=O stretching ketone	Lowered to ca. 1680 cm^{-1} by conjugation. Raised by ca. 35 cm^{-1} per atom decrease in ring size below 6-membered ring.
1710	C=O stretching carboxylic acid (dimer)	Band appears near 1760 cm^{-1} in monomer (rarely observed). Shifts to 1610-1550 cm^{-1} in carboxylate anion (salts).
1690-1650	C=O stretching amide	Associated forms have C=O stretching ca. 30-40 cm^{-1} lower. NH_2 bending also makes a strong contribution to the 1650-1600 cm^{-1}.
1650-1600	C=C stretching alkene	Frequency is increased for exocyclic C=C with decreasing ring size; the opposite occurs for endoyclic C=C except for cyclopropene; absorption occurs at lower frequency in conjugated alkenes. Polar groups increase band intensity.
1640	C=N stretching	This band is usually weak (compared to C=O).
1600 and 1500 also 1580 and 1450	C=C stretching aromatic nuclei	Variable intensity; stronger when conjugated or electron donor groups are attached. Other systems also absorb in this region (e.g., NH_2 bending).
1600	$-NH_2$ bending	Useful to identify 1° amines and amides.
1540	-NH- bending	Useful to identify 2° amines and N-mono-substituted amides; may be weak.
1520 and 1350	$-NO_2$ asym. & sym. stretching	This pair of bands is usually quite intense.
1465	$-CH_2-$ bending	
1450 and 1380	$-CH_3$ bending	The lower frequency band is especially useful to detect methyl groups. Geminal methyl groups give rise to a doublet (1385 and 1365 cm^{-1}).
1410	$-CH_2CO-$	For a methylene group attached to a carbonyl group.
1325	-CH- bending	Usually weak and often unreliable.
1200	Ar-O	These strong bands are commonly assigned to C-O stretching. The position is shifted with unsaturation and branching, and over-lapping bending vibrations often make interpretation uncertain.
1150	-C-O-	
1100	-CH-O-	
1050	$-CH_2-O-$	
1050	RSOR' (sulfoxide)	Strong
1330 and 1140	RSO_2R' (sulfone)	Strong doublet (coupled oscillator)
1380 and 1170	RSO_3R'	Strong doublet (coupled oscillator)

cm^{-1}	Functional group	Comments
970	 C-H bending	Useful to distinguish E (trans) 1,2-disubstituted alkenes from Z (cis) isomers.
890	$R_2C{=}CH_2$ C-H bending	This strong band identifies a terminal methylene group. It is raised by 20-80 cm^{-1} if bonded to an electronegative atom or group.
815	$R_2C{=}CHR$ C-H bending	Moderately strong band to characterize a trisubstituted double bond.
730-675	 C-H bending	Usually broad and sometimes absured by solvent absorption (C-Cl).
750 and 690	monosubstituted phenyl C-H bending 5 adjacent H's	These are usually the strongest bands below 900 cm^{-1}. Electron withdrawing groups suc as $-NO_2$ increase the frequency by ca. 30 cm^{-1}. Chlorinated solvents obscure some of these bands.
750	*ortho*-disubst. phenyl C-H bending 4 adjacent H's	
780 and 700	*meta*-disubst. phenyl C-H bending 3 adjacent H's	
825	*para*-disubst. phenyl C-H bending 2 adjacent H's	

Infrared Regions Obscured by Solvents

Solvent	Region(s) Obscured
CCl_4	840-700 cm^{-1}
$CHCl_3$	3000 cm^{-1} 1200 cm^{-1} 840-700 cm^{-1}
CS_2	1600 - 1400 cm^{-1}

* Values mainly from dilute solutions in relatively nonpolar solvents. They often change with solvent and in liquid film or solid-state spectra.

Learning Organic Chemistry Reactions with Flashcards

A lot of students struggle with learning reactions. It is important to accept that you literally have to know the reactions backwards and forwards in detail. A great way to learn reactions is using flash cards.

First a few tips about making the cards.

1. Make several versions of each reaction. Do not draw generic structures (meaning structures with the functional group surrounded by R groups). Pick real molecules from your text and notes. The more you vary them the more flexible you will become.

2. Do not make marks on your cards. Do not write mechanisms on the cards. You will start the recognize the reaction by the marks rather than the reaction

In practicing it works well to do the following.

1. The first few times you go through your reactions write out the mechanisms in a very detailed way. Try to do it from memory.

2. When the mechanisms start to flow more rapidly, see if you can work through the mechanisms mentally - sort of like a high speed mental movie of what you have learned.

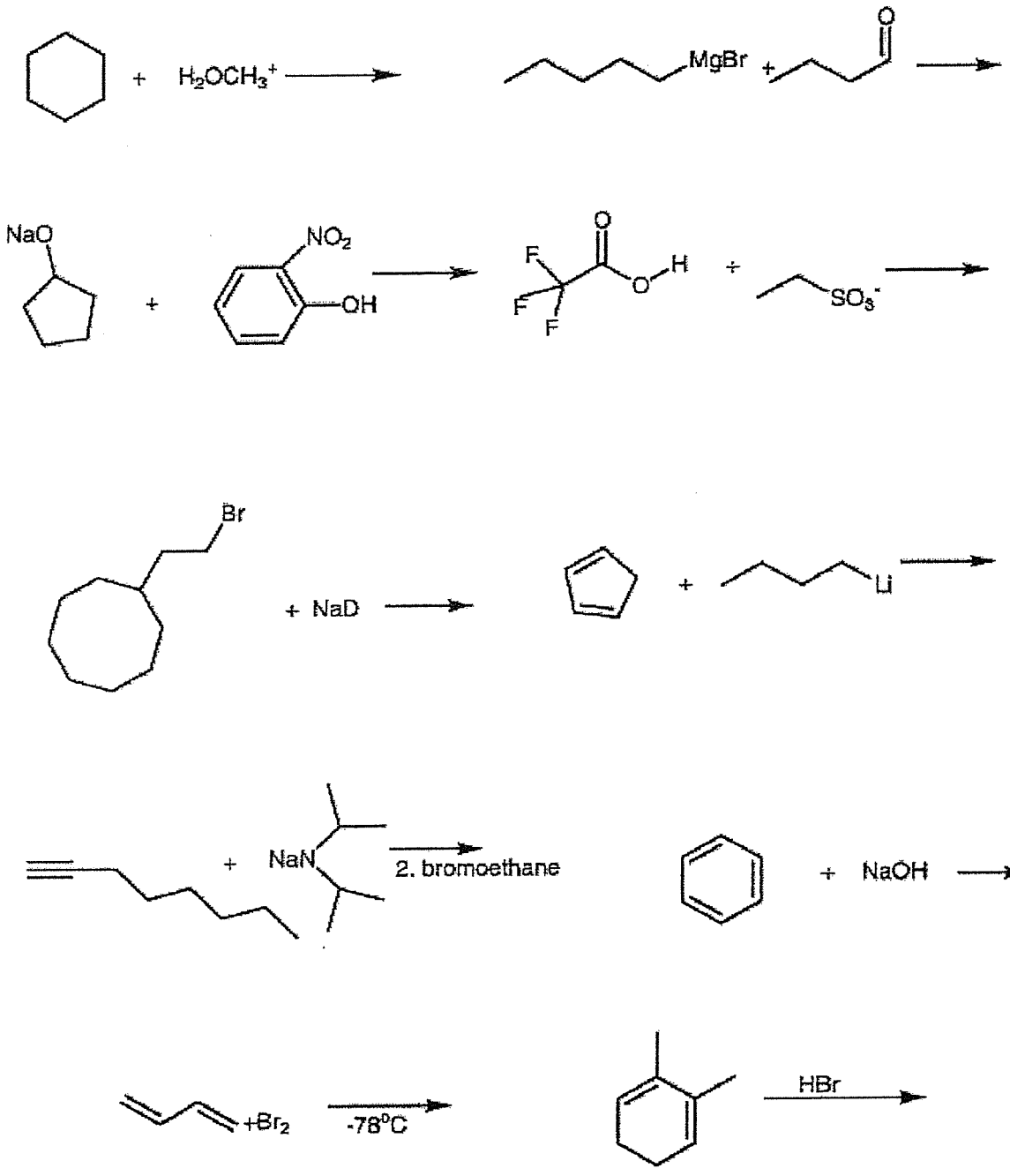
3. When the you can do mental mechanisms and get the right products, you need to start learning the reactions synthetically. Re-sort the cards according to the type of functional group you are making. Put all the alcohol products in one pile, all the haloalkane products in another. Start looking at these reactions to determine what makes each one unique. For example, does it give anti-markovnikov or markovnikov products? Is the reaction accompanied by rearrangement? Is it a syn additon or an anti? etc.

4. When you have the reactions sorted out synthetically, see if you can come up with the reagents that would yield a given product. In some cases there will be more than one way to make a given product.

5. When you have your cards mastered backwards and forwards, trade with a friend. Seeing a new set of substrates will challenge you a bit and get you ready for the exam.

In my opinion, this is one of the best ways to learn the bulk of the

Flash Cards Sheet no. 1



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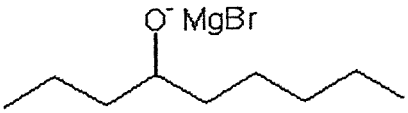
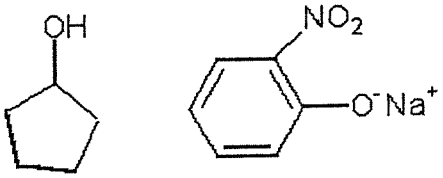
Flash Cards no. 1 - Products Answers are in their relative positions on the cards



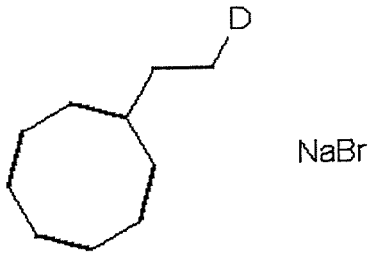
No Reaction - There is nothing to protonate in the cycloalkane

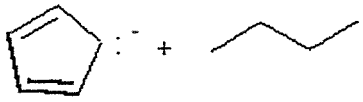
Attacking most positive site in molecule



No Reaction - weaker acid and base going to stronger acid and base - see chart

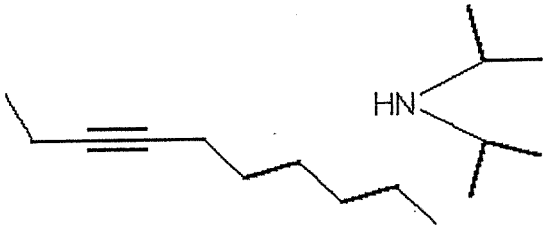
The second structure has resonance stabilization - can you draw structures?





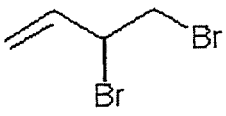
The first structure has resonance stabilization - can you draw structures?

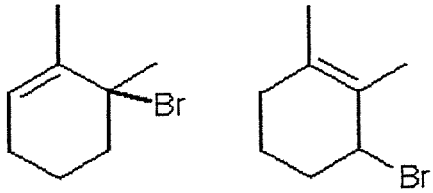
Attacking most positive site in molecule - SN2 type reaction



No Reaction - weaker acid and base leading to stronger acid and base

proton abstraction from the terminal alkyne followed by SN2 reaction on bromoethane





Major, kinetic conditions

No conditions specified - so both products shown

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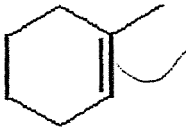
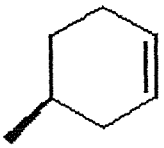
Chem 211 Flashcards no. 2 Reactants

Watch out this first one is hard!!!

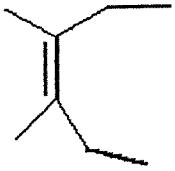
HCl



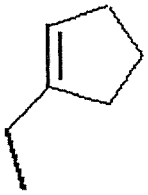
+ HBr



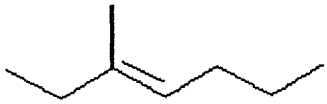
+ Br_2



+ Cl_2

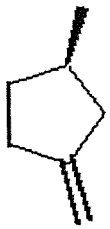


+ Cl_2 / H_2O



+ Br_2 / H_2O

+ HCl / H_2O



+ $Hg(OAc)_2$ / 1. H_2O 2. $NaBH_4$

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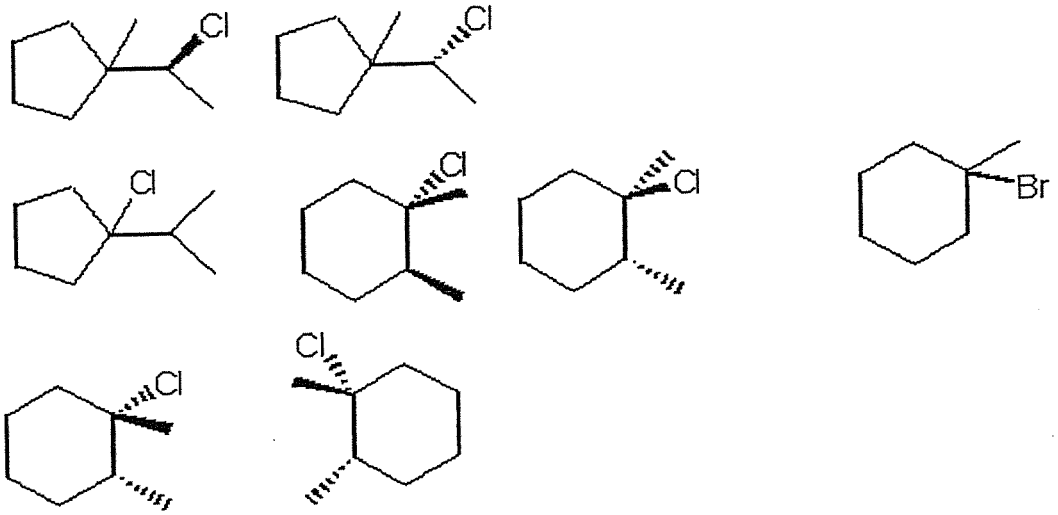
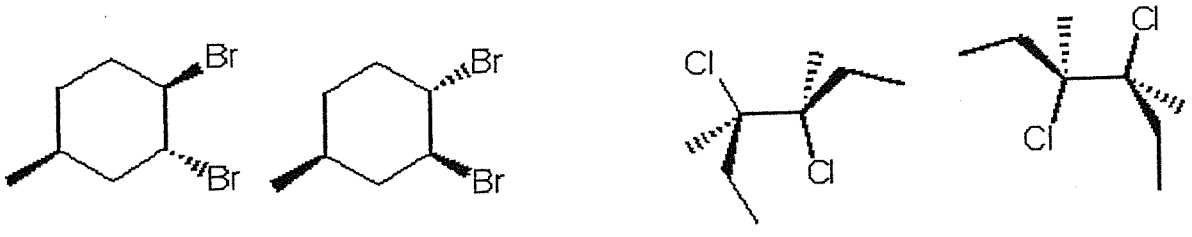
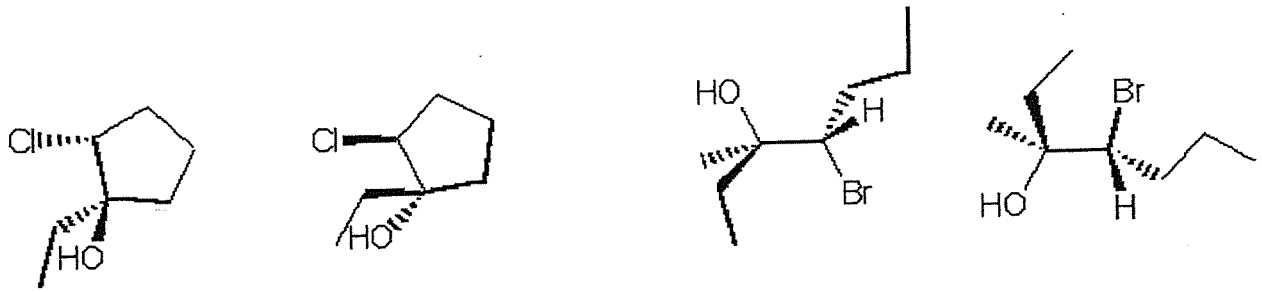
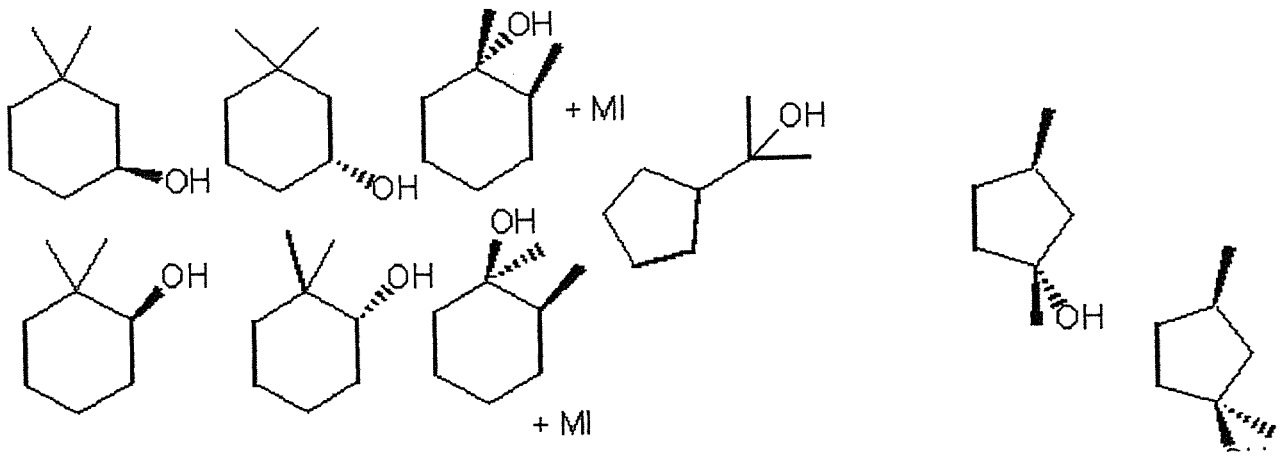
Chem 211 Flashcards no. 2 - products



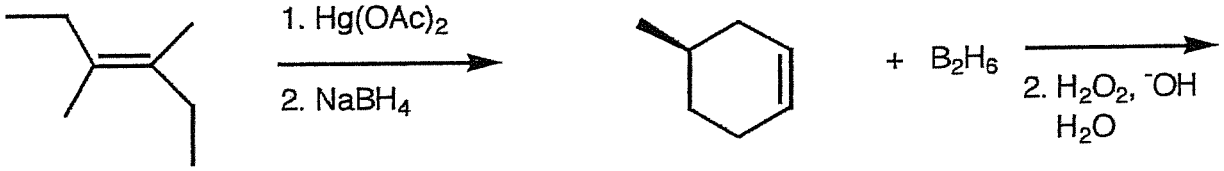


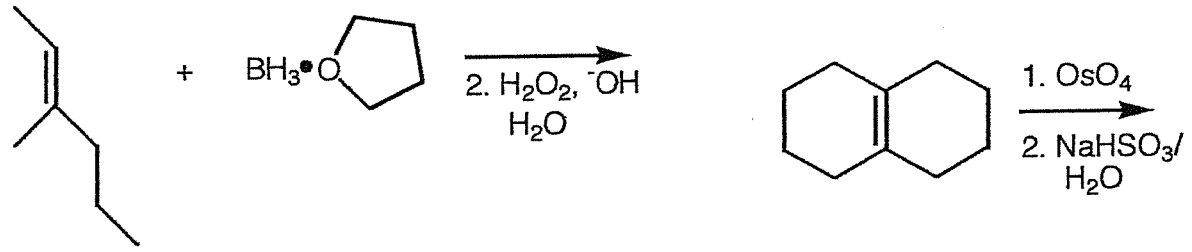


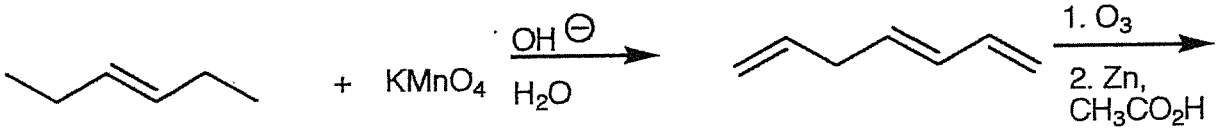


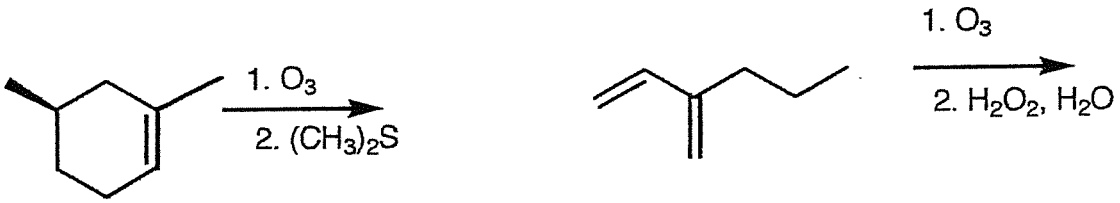
Please note: MI = mirror image, ie. enantiomer

Chem 211 Flashcards no. 3 Reactants

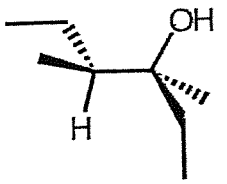


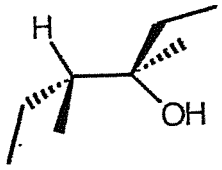


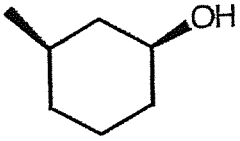


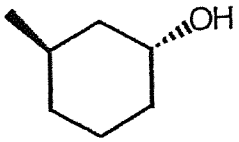


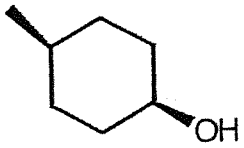
Chem 211 Flashcards no. 3 - Products

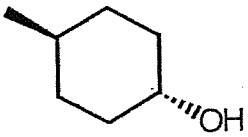


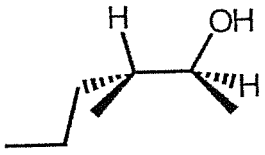


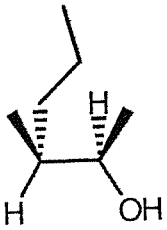


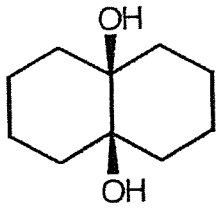


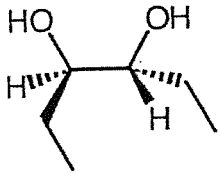


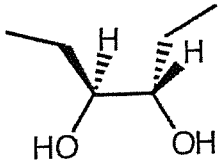


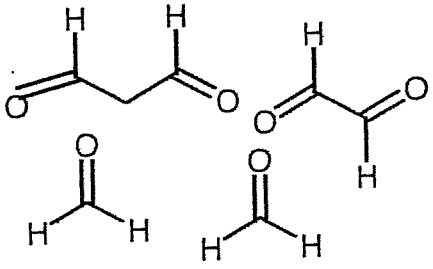


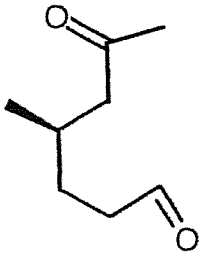


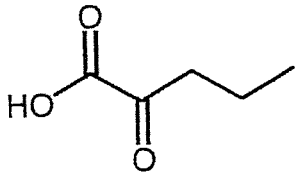






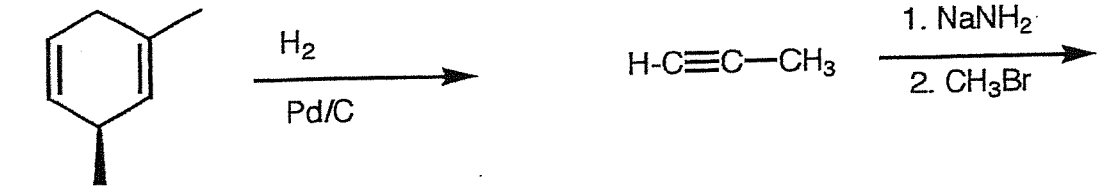


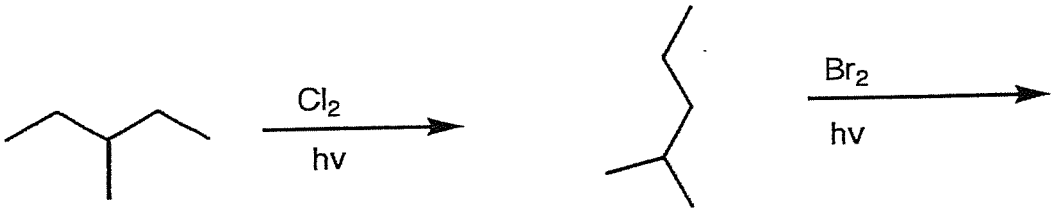


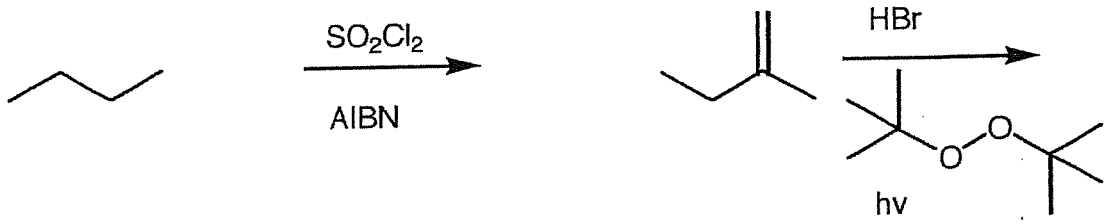


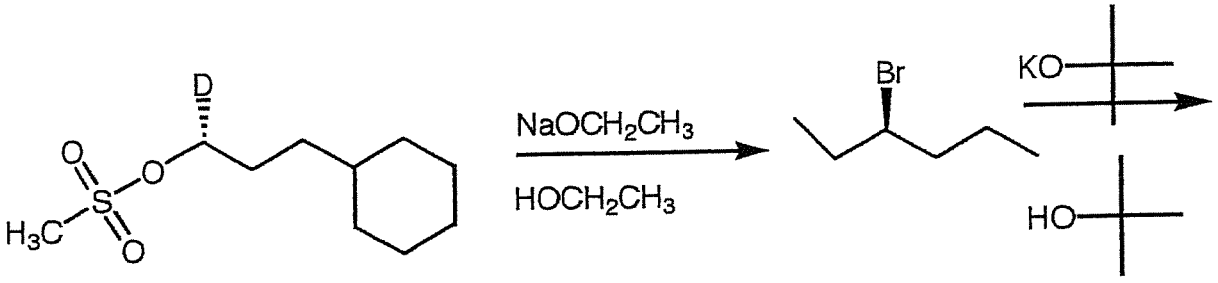
+ 2 formic acid
(ethanoic acid)

Chem 211 - Flashcards no. 4 - Reactants

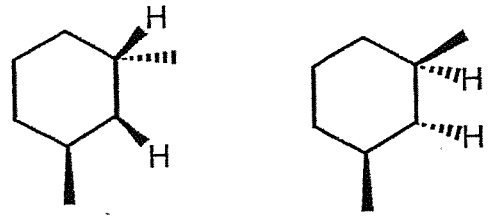


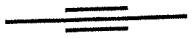


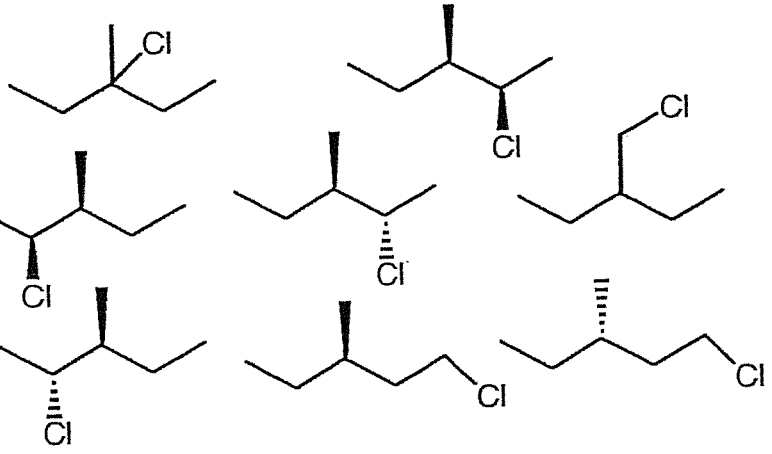


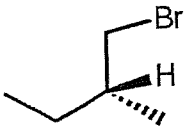


Chem 211 - Flashcards no. 4 - Products









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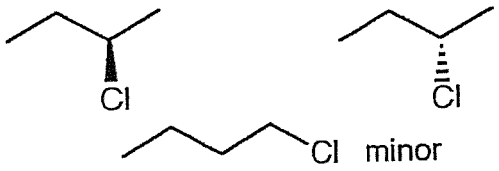

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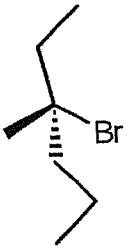
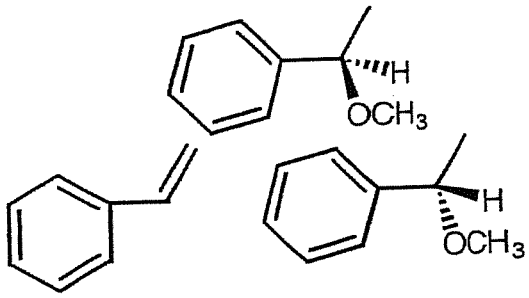
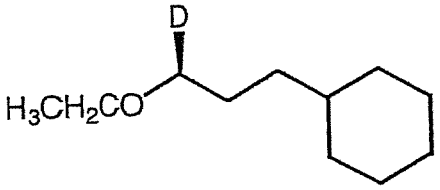
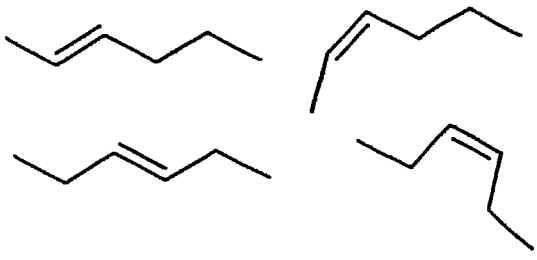


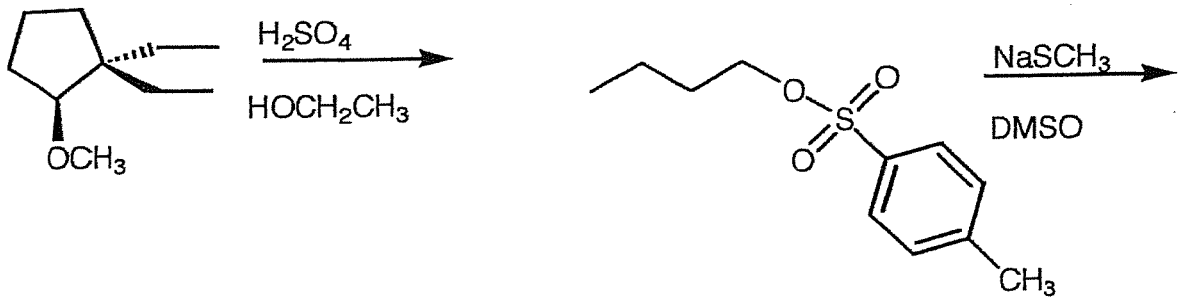
+ MIrror image

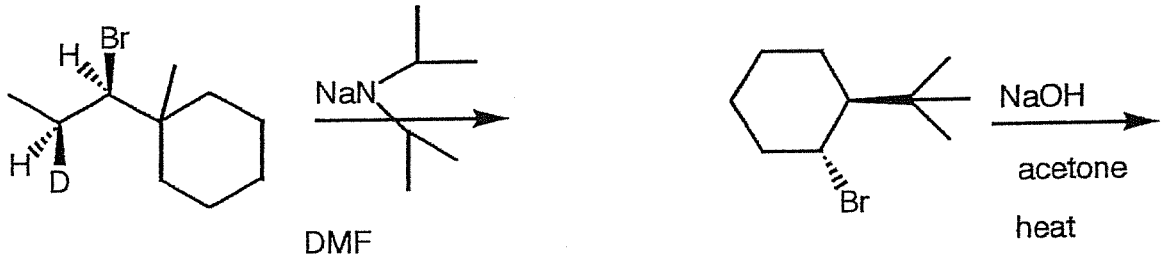


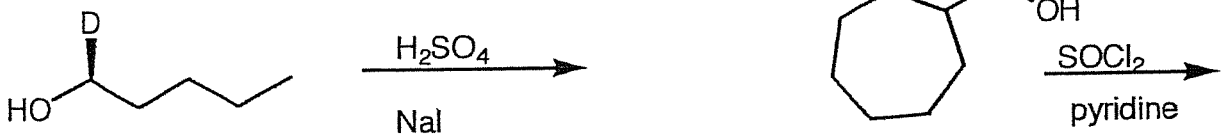


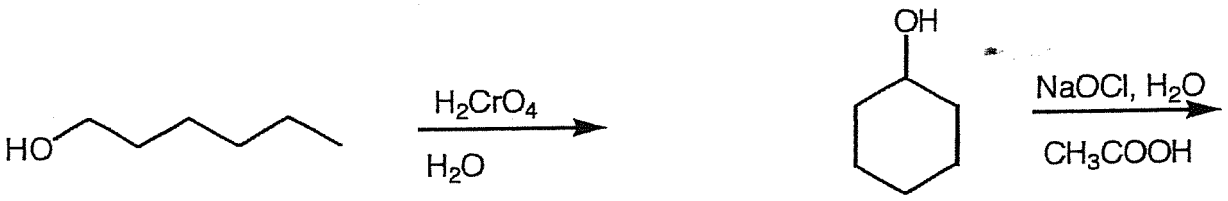


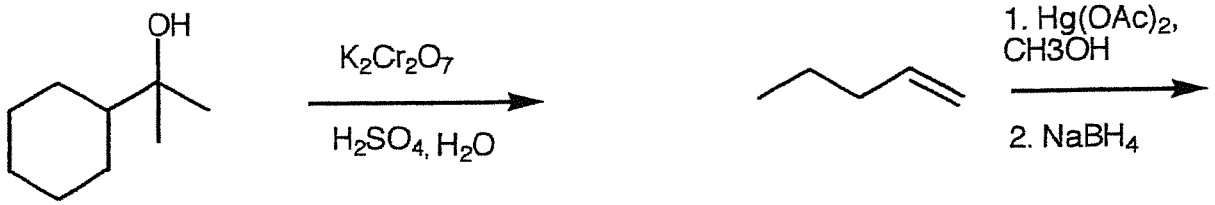
Chem 211 - Flashcards no. 5 - Reactants





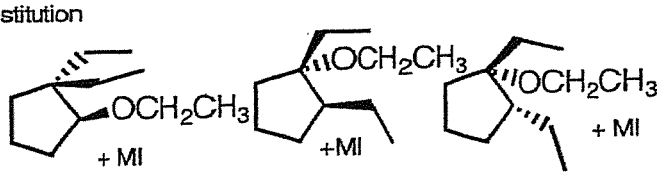


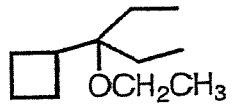




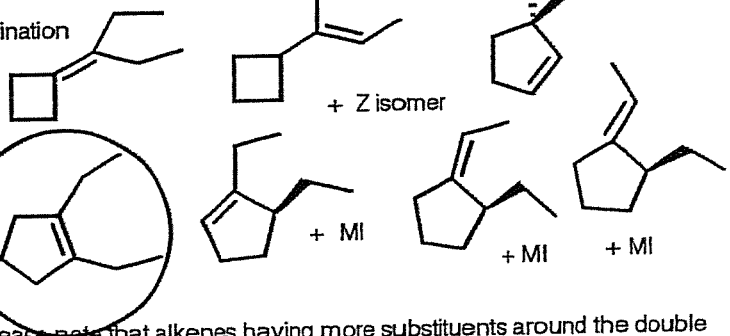
Chem 211 - Flashcards no. 5 - products

substitution

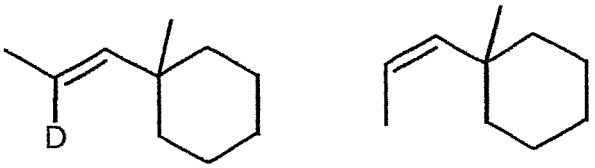




elimination

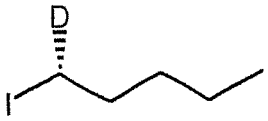


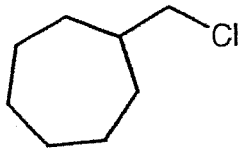
Please note that alkenes having more substituents around the double bond tend to be most abundant so the circled alkene is most likely to be major

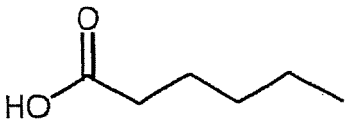


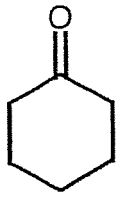
E_2 - carefully consider stereochemistry of elimination

no reaction, Br not in proper position for elimination - E_2 possible minor amount of Sn_2

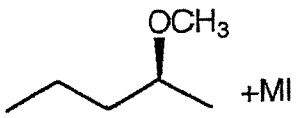






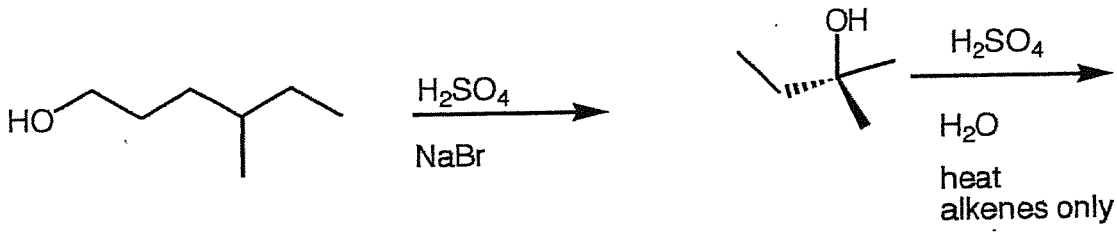


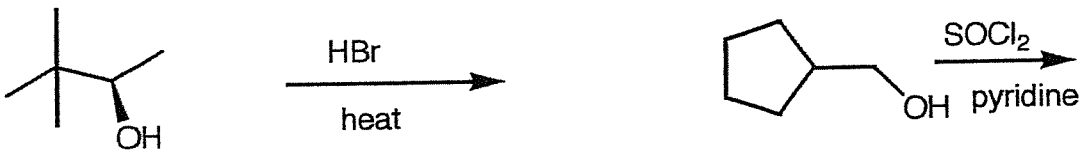
oxidation - see lab notes last Wednesday

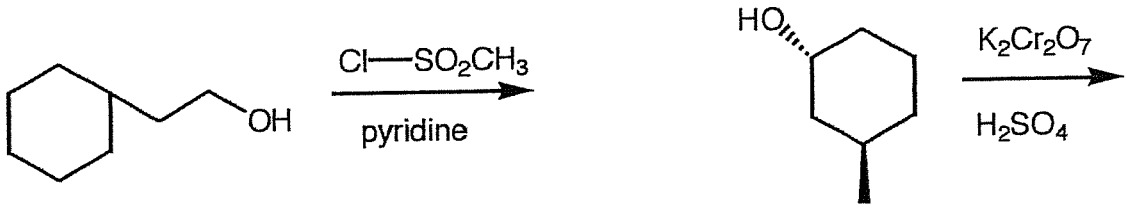


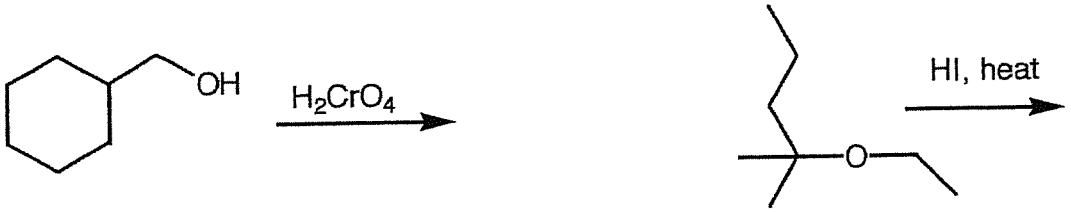
No reaction - tertiary alcohol
no beta hydrogen - oxidations
are fundamentally elimination reactions

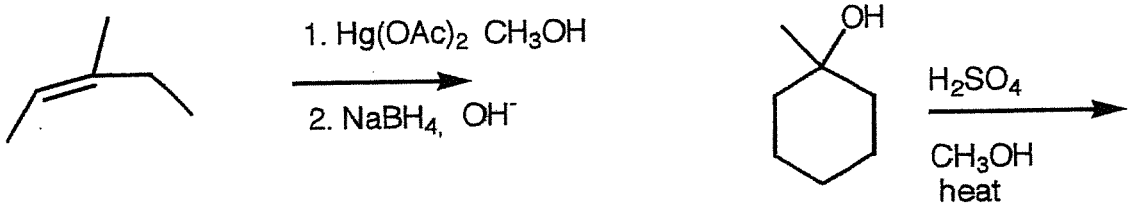
Chem 211- Flashcards no. 6 - Reactants



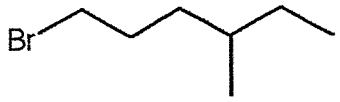


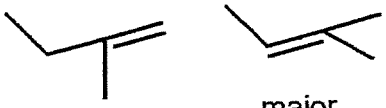




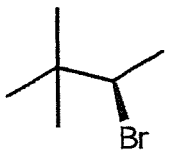


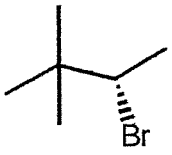
Chem 211 - Flashcards no. 6 - Products

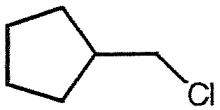


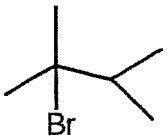


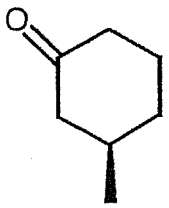
major

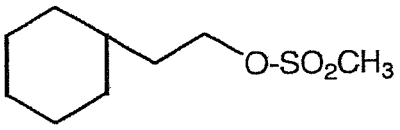




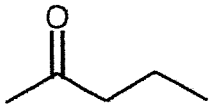


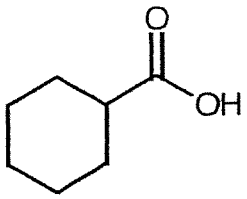


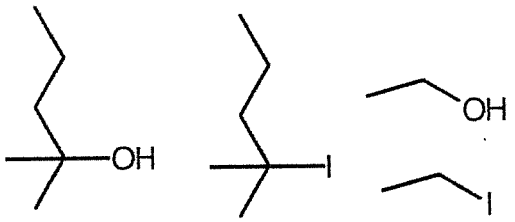


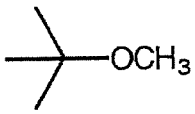


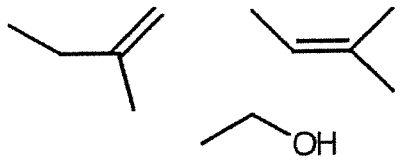
No reaction - no beta hydrogen

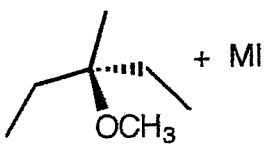


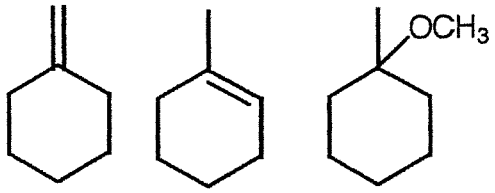




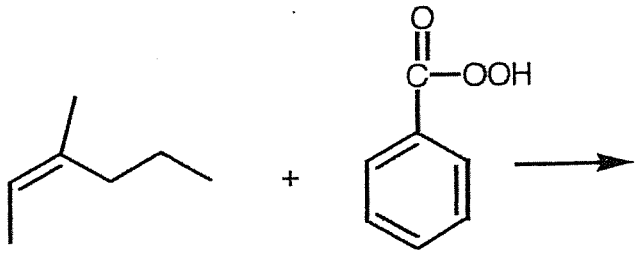


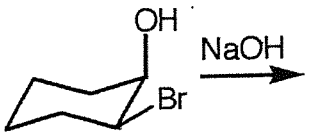


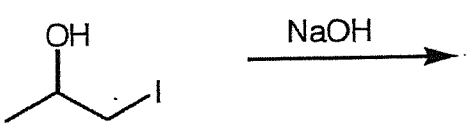


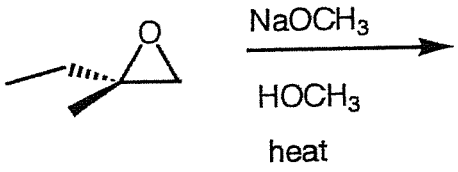


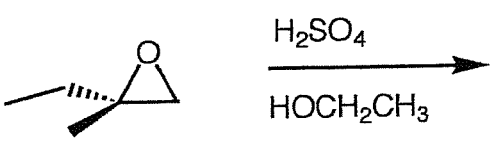
Chem 211 Flashcards no. 7 - reactants

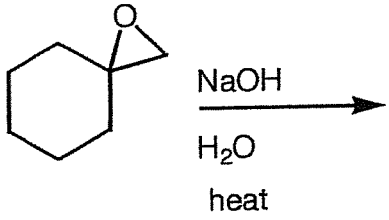




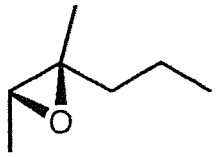






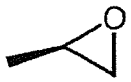


Chem 211 - Flashcards no. 7 products



+ MI

no reaction - can't assume anti conformation



+ MI