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Designing Exercises to Determine the Structural Formula of Organic Compounds Based on the Experimental Data

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Abstract This paper introduces the way to design exercises to determine the structural formula of organic compounds based on the experimental data. They are structure, physical properties, typical chemical properties, synthesis methods and application. From that the authors have built the scheme to design exercises. On that basis, the authors compiled some exercises which are used for teaching and learning organic chemistry in university and high school.

Keywords: *designing exercise, structural formula, organic compound, experimental data, teaching and learning organic chemistry, mechanisms of reactions*

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1. Introduction

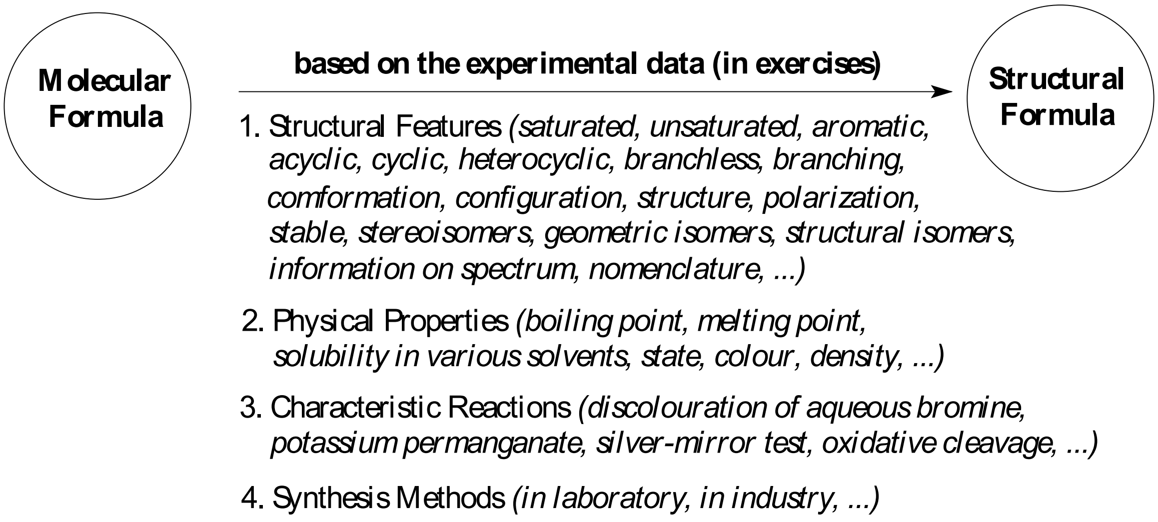
Designing exercises is essential in teaching chemistry, an indispensable activity of chemistry teacher at the universities and high schools. Organic chemistry exercises have more interesting contents, special exercises for identified structural formula of organic compounds will require students to have a basic knowledge of organic chemistry such as stereochemistry, reaction mechanisms or organic synthesis, etc [1].

Exploiting the experimental data to determine the structure of organic compounds are important skills to help students practice on scientific research in the university. Solving this exercises will help students to form experimental thinking in teaching of chemistry and research of organic chemistry.

2. Method – Desining Exercises

In order to determine the structural formula of organic compounds must first identify the components of qualitative and quantitative elements present in organic compounds, mean that molecular formula. Since it is based on experimental data on the molecular structure, chemical and physical properties of organic compounds and synthetic methods, we can argue to determine correctly structural formula of the organic compounds [2].

General scheme to design exercises as shown below.



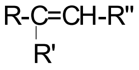
Molecular Formula

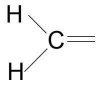
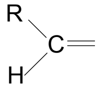
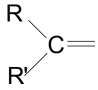
based on the experimental data (in exercises)

Structural Formula

1. Structural Features *(saturated, unsaturated, aromatic, acyclic, cyclic, heterocyclic, branchless, branching, conformation, configuration, structure, polarization, stable, stereoisomers, geometric isomers, structural isomers, information on spectrum, nomenclature, ...)*
2. Physical Properties *(boiling point, melting point, solubility in various solvents, state, colour, density, ...)*
3. Characteristic Reactions *(discolouration of aqueous bromine, potassium permanganate, silver-mirror test, oxidative cleavage, ...)*
4. Synthesis Methods *(in laboratory, in industry, ...)*

Table 1. Some typical chemical properties of substances [3,4]

Order	Properties of A	Structure of A
1	(A) + Na $\rightarrow$ H_2	- OH (alcohol, phenol) - COOH (acid)
2	(A) + NaOH (aq) (at r.t.p.)	- OH (phenol). - COOH (acid). - Salts of weak base. ($RCOONH_4$, $RCOONH_3R'$). - NH_2RCOOH (amino acid). - Dipeptide and polypeptide. (Hydrolysis in alkali).
3	(A) + soln. of NaOH (heat)	- RCOOR' (ester) - RX (halogen derivatives, X does not link directly with the aromatic ring)
4	(A) + H_2 (Ni, heat)	- Unsaturated compounds (double bonds, triple bonds). - Unstable rings (three-member rings or four-member rings). - RCHO (aldehyde) - RCOR' (ketone) - Glucose, fructose, maltose.
5	(A) + $LiAlH_4$/ether	- RCOOH (carboxylic acid) - RCOOR' (ester)
6	(A) + dil. soln. of HCl, H_2SO_4	- RNH_2 (amine). - NH_2RCOOH (amino acid). - Salt of weak acid. - Di and polysaccharide (hydrolysis in acid). - Di and polypeptide (hydrolysis in acid).
7	(A) + soln. of $AgNO_3/NH_3$ $\rightarrow$ Ag (s), white	- RCHO (aldehyde). - HCOOH (formic acid). - HCOOR' (ester of formic acid). - $HCOONH_4$, HCOONa (salt of formic acid). - Glucose, fructose, maltose.
8	(A) + soln. of $AgNO_3/NH_3$ $\rightarrow$ yellow precipitate.	- Acetylene and alk-1-yne: R-C≡CH. - Organic compound with fist triple bonds: R-(C≡CH)x.
9	(A) + $Cu(OH)_2$ (at r.t.p) $\rightarrow$ solution with typical color.	- Vicinal diol - Carboxyl group –COOH. - More than or equal to 2 peptide bonds (Biuret Reaction). *Note*: - *If A is vicinal diol* $\rightarrow$ *blue-colored coordination complexes* - *If A has –COOH group, A will dissolve* $Cu(OH)_2$ $\rightarrow$ *blue-colored solution* (Cu^{2+} *in water).* - *If A has more than or equal to 2 peptide bonds (tripeptit, polipeptit, protein,...)* $\rightarrow$ *violet-colored coordination complexes in an alkaline solution.*
10	(A) + $Cu(OH)_2/OH^-$ $\xrightarrow{heat}$ Cu_2O (brick-red)	- RCHO (aldehyde). - HCOOH (formic acid). - HCOOR' (esters of formic acid). - $HCOONH_4$, HCOONa (salts of formic acid). - Glucose, fructose, maltose.
11	(A) + Br_2 *(aq)* $\rightarrow$ discoloration	- Unsaturated compounds (double bonds, triple bonds). - Unstable rings (three-member rings). - Phenol, aniline (white precipitate). - RCHO (aldehyde) - Glucozơ, fructozơ, mantozơ.
12	(A) + $KMnO_4$ *(aq)* $\rightarrow$ discoloration	- Unsaturated compounds (double bonds, triple bonds). - RCH_2OH (primary alcohol). - RCHO (aldehyde). - Glucose, fructose, maltose.
13	(A) + $KMnO_4$ *(aq)* $\xrightarrow{heat}$ discoloration	- Unsaturated compounds (double bonds, triple bonds). - RCH_2OH (primary alcohol). - RCHO (aldehyde) - Glucose, fructose, maltose. - Homology of benzene.
14	(A) + $KMnO_4/H^+$ $\rightarrow$ RCOOH + CO_2	R-CH=CH_2 R-C≡CH
15	$(A) + KMnO_4/H^+ \rightarrow \begin{cases} RCOR' \\ R''COOH \end{cases}$	 $R\text{-}\underset{\underset{R'}{\vert}}{C}\text{=CH-R''}$

Order	Properties of A	Structure of A
16	$(A) + KMnO_4/H^+ \rightarrow \begin{cases} RCOOH \\ R'COOH \end{cases}$	R-CH=CH-R' R-C≡C-R'
17	(A) + soln. of HNO_3/H_2SO_4 (conc.) → yellow liquid that does not dissolve in water.	Arenes
18	$(A) + O_3 \begin{cases} \xrightarrow{Zn/H_2O} \text{HCHO (Formaldehyde)} \\ \xrightarrow{H_2O_2} \text{HCOOH (Formic acid)} \end{cases}$	
19	$(A) + O_3 \begin{cases} \xrightarrow{Zn/H_2O} \text{RCHO (Aldehyde)} \\ \xrightarrow{H_2O_2} \text{RCOOH (Carboxylic acid)} \end{cases}$	
20	$(A) + O_3 \begin{cases} \xrightarrow{Zn/H_2O} \text{RCOR' (Ketone)} \\ \xrightarrow{H_2O_2} \text{RCOR' (Ketone)} \end{cases}$	

Summarizing some typical chemical properties in Table 1.

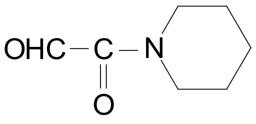
3. Sample Problems

Example 1

From pepper isolated alkaloid piperine **A** ($C_{17}H_{19}NO_3$) is a neutral substance [3]. Ozonolysis of compound **A** formed substances: ethanedial (ethane-1,2-dione), **B**, **D**. Hydrolysis of **B** formed OHC-COOH and six-member heterocyclic compounds piperidine ($C_5H_{11}N$). Given **D** reacts with concentrated solution of HI to form 4,5-dihydroxybenzandehyde. Identify structural formulae of **A**, **B**, **D**. How many stereoisomers of **A** are there?

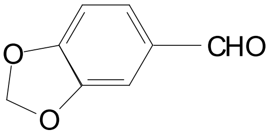
Solution:

- Hydrolysis of **B** formed OHC-COOH and piperidine, inferred **B** to contain the O=C-N- bond (nitrogen atom belongs to six-member ring). Structural formula of **B** is



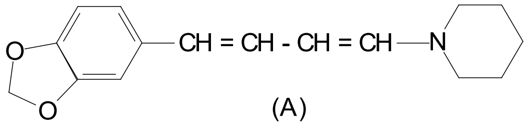
(B)

- D reacts with HI to form 4,5-dihydroxybenzandehyde. Structural formula of **D** is



(D)

- Ozonolysis of compound **A** formed ethanedial, inferred **A** contains the =CH-CH= group.



(A)

- Compound **A** has 2 double bonds C=C, so there are 4 geometric isomers: ZZ, EE, ZE, EZ.

Example 2

Given an organic compound **X** is created by three chemical elements, has a molar mass of 282 g/mol. Mass analysis of **X** shows 17.02% oxygen. Complete combustion **X** formed moles of CO_2 twice as much as moles of H_2O. Let **X** reacts with excess $(i\text{-}C_3H_7O)_3Al$ / *i*-C_3H_7OH to form compound **Y** which has a molar mass of 288 g/mol. When reduction or oxidation ozonolysis to form the only compound **Z** which has a molar mass of 314 g/mol. Reduction **Z** by $NaBH_4$, then the resultant product is oxidized with $NaIO_4$ to form mixture of *o*-$C_6H_4(CHO)_2$ and $OHC(CH_2)_5CH(OH)(CH_2)_2CHO$. On the other hand, treatment **X** with $NaNH_2$ / DMF to form $\mathbf{X_1}$ ($C_{18}H_{18}O_3$). Let X_1 reacts with H_2 / Pd, then heated resultant product with conc. H_2SO_4 to give $\mathbf{X_2}$ ($C_{18}H_{20}O$).

a) Draw the structural formula of **X**, **Y**, **Z**, $\mathbf{X_1}$ and $\mathbf{X_2}$.

b) Explain the formation mechanism of $\mathbf{X_1}$ from **X**.

Solution:

a) Burning **X** for $n_{CO_2} = 2n_{H_2O}$ → The number of carbon atoms equal the number of hydrogen atoms.

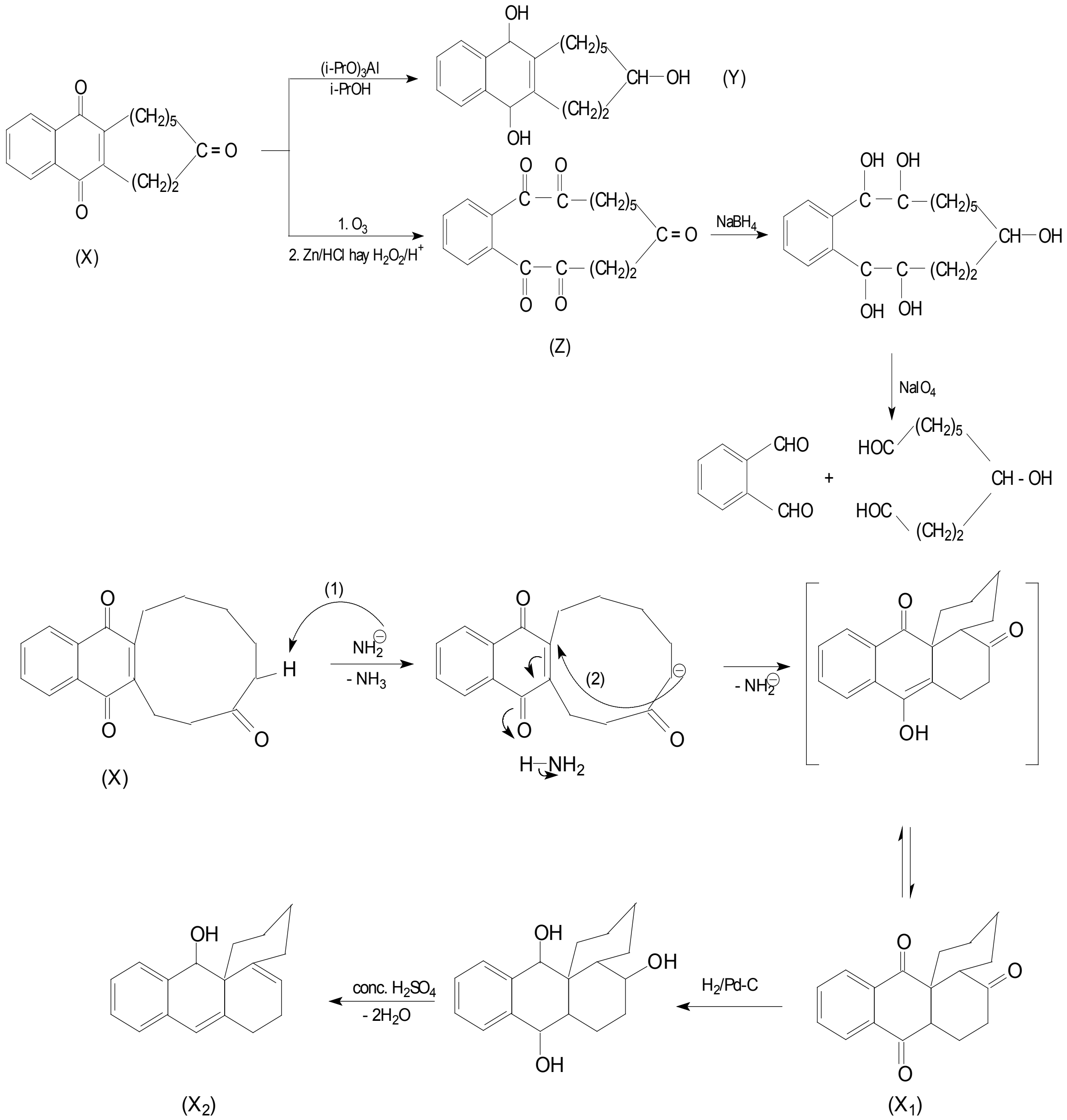
Call the molecular formula of **X** is $C_xH_xO_z$ → $z = \dfrac{282x17.02}{16x100} = 3$ → $M_X = 13x + 16 \text{ x } 3 = 282$ → x = 18 → The molecular formula of X is $C_{18}H_{18}O_3$.

For $M_Y - M_X = 288 - 282 = 6$ → The molecular formula of **Y** compared to **X** to increase 6H after the Meerwein–Ponndorf–Verley (MPV) reduction [5], proving that **X** has 3 carbonyl groups (C = O).

We have transformed the following:

$$X(C_{18}H_{18}O_3) \xrightarrow{(i\text{-}C_3H_7O)_3Al/(CH_3)_2CHOH} Y(C_{18}H_{24}O_3).$$

The oxidation ozonolysis of X to form the only compound Z which has $M_Z - M_X = 32$ → Proving that oxidation ozonolysis of **X** which had gained more 2 oxygen atoms to form **Z**. Therefore, **X** has a double bond (C = C) in the ring and in this double bond is no longer hydrogen atom. The structural formula of **X**, **Y**, **Z**, $\mathbf{X_1}$ and $\mathbf{X_2}$ are determined by the following diagram:



b) Mechanism of forming X_1 from X according to Michael addition reaction through 2 steps:

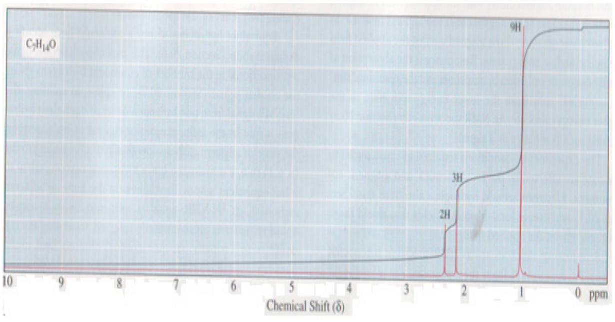
Step (1): $NaNH_2$ attacks on H_α to form carbanion.

Step (2): Carbanion attack on carbon to produce ring with 6 sides.

Example 3

Following is the ^{1}H-NMR spectrum [6] for compound **X** of molecular formula $C_7H_{14}O$.

Propose a structural formula for compound **X**.



Solution:

From the ^{1}H-NMR spectrum to the structural formula for compound **X**.

- *Examine the molecular formula, calculate the degree of unsaturation (DU), and deduce what information you can about the presence or absence of rings or* π *- ponds*. The molecular formula $C_7H_{14}O$ that has DU = 1 $\rightarrow$ the compound contains 1 ring or 1 π - pond.

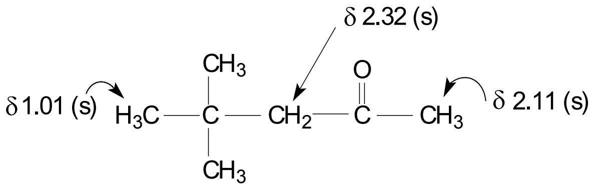
- *Count the number of signals to arrive at a minimum number of different sets of hydrogens in the compound.* There are three signals, therefore, three sets of equivalent hydrogens.

- *Use the line of integration and the molecular formula to determine the number of hydrogens in each set.* Reading from right to left, signals are in the ratio 9H : 3H : 2H.

- *Examine the NMR spectrum for signals characteristic of the following types of hydrogens. Keep in mind that these are broad ranges and that hydrogens of each type may be shifted either farther upfield or farther downfield depending on details of molecular structure.*

The singlet at δ 1.01 is characteristic of a methyl group adjacent to an *sp*^{3} hybridized carbon. The singlets at δ 2.11 and 2.32 are characteristic of alkyl groups adjacent to a carbonyl group.

- *Examine splitting patterns for information about the number of nonequivalent neighboring hydrogens.* All signals are singlets (s).
- *Write a structural formula consistent with the previous information*. The compound **X** is 4,4-dimethylpentan-2-one.



4,4-Dimethylpentan-2-one

Example 4

Safrole **A**, $C_{10}H_{10}O_2$, a sweet-smelling liquid isolated from oil sassafrass, given the following properties:

- It does not dissolve in NaOH or give a color with $FeCl_3$.
- It adds 1 eq of H_2 on catalytic hydrogenation.

Reductive ozonolysis affords $H_2C{=}O$ and **B** ($C_9H_8O_3$) that gives a positive Tollens' test.

- Oxidation of **A** with $KMnO_4$ gives an acid **E** (MW = 166) which gives no color with $FeCl_3$.
- When **E** is refluxed with conc. HI, $H_2C{=}O$ and 3,4-dihydroxybenzoic acid are isolated and identified.

Deduce the structures of **A**, **B** and **E**.

Solution:

DU (degree of unsaturation) = 6, four of which are due to a benzene ring.

Since (A) does not dissolve in NaOH or give a color with $FeCl_3$, it is not a phenol.

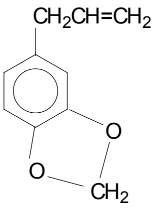
Formation of $H_2C{=}O$ on ozonolysis means that **A** has a chain with a terminal $=CH_2$ grouping, and since **B** is an aldehyde (positive Tollens' test), the grouping is $-CH{=}CH_2$. The double bond accounts for the fifth DU.

E is a monocarboxylic acid formed by complete oxidation of the alkenyl side chain, and its molecular weight is 166.

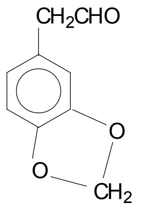
No other C can be directly attached to the ring because it would have oxidized, giving a dicarboxylic acid.

The two remaining Os must be present as ether linkages probably present as a ring, the sixth DU, fused to the benzene ring. This is confirmed by isolating $H_2C{=}O$ and 3,4-dihydroxybenzoic acid on cleavage with HI. This fused ring is actually a stable acetal.

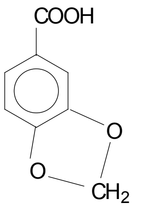
The molecular formula of **E** is $C_8H_6O_4$. The acetal ring and the benzene ring account for seven Cs, leaving three Cs for the alkenyl side chain. The structures for **A**, **B** and **E** are:



(A)



(B)



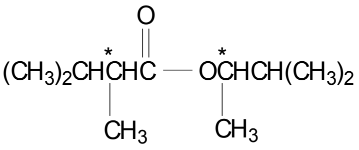
(E)

Example 5

A pleasantly smelling, optically active compound **F** (MW = 186) [9]. It does not react with Br_2 in CCl_4. Hydrolysis of **F** gives two optically active compounds, **G**, which is soluble in NaOH, and **H**. Compound **H** gives a positive iodoform test, and on warming with conc. H_2SO_4 gives **I** with no diastereomers. When the Ag^+ salt of **G** is reacted with Br_2, racemic **J** is formed. Optically active **J** is formed when **H** is treated with tosyl chloride (TsCl) and then NaBr. The IR spectrum of **F** shows a single C=O stretching peak. Give structures of **F** through **J** and explain your choices.

Solution:

F is a saturated monoester with MW = 186 (no Br_2 reaction). We can logically determine the number of Cs and the molecular formula by subtracting the mass of the two Os and dividing the remainder by 14, the mass of CH_2: (186 - 32)/14 = 11. To complete the mass there must be 22 Hs. The molecular formula is $C_{11}H_{22}O_2$. The acid **G** has one more C than the alcohol **H** because it is degraded by one C in the Hunsdiecker reaction [7,8] ($RCOO^-Ag^+ + Br_2$) to **J** which is also made from **H** with no change in C content. **H** is a methyl carbinol, $CH_3CH(OH)R$, because it gives a positive iodoform reaction and, in order to be chiral, must have at least four Cs. However, **H** has five Cs because the alkene, **I**, obtained on dehydration (warm conc. H_2SO_4), must have two Mes on one of the doubly bonded Cs to avoid *cis-trans* isomerism. **I** is $CH_3CH{=}C(CH_3)_2$ with five Cs and **G** had six Cs. **H** is $CH_3CHOHCH(CH_3)_2$ and is converted to **J**, $CH_3CHBrCH(CH_3)_2$, through the tosylate, $CH_3CH(OTs)CH(CH_3)_2$, with no change in configuration, by an S_N2 reaction with Br^-. Consequently, **H** and **J** have inverted configurations. The skeleton of the alkyl group of **G** is the same as **H**. Replacing Br of **J** by COOH gives the structure of **G**, $(CH_3)_2CHCH(CH_3)COOH$. **F** is one of the four possible enantiomers of



$$(CH_3)_2CH\underset{CH_3}{\overset{*}{C}}H\overset{O}{\overset{\|}{C}}-O\underset{CH_3}{\overset{*}{C}}HCH(CH_3)_2$$

4. Conclusions

Above are some examples of building exercises to determine the structure of organic compounds based on empirical data. Because empirical data on the structure is very rich so there are many forms of this type of exercise. In resolving the types of exercises will improve the students' thinking, especially the analysis of the reaction mechanism and the structure of organic compounds.

Acknowledgements

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References

[1] Hass, M.A. Student-Directed learning in organic chemistry laboratory. *J. Chem. Educ.* 2000, 77(8), 1035-1038.

[2] Ram, P. Problem-based learning in undergraduate education. *J. Chem. Educ.* 1999*,* 76(8), 1122-1126.

[3] Giac C.C. *The Diamonds in Chemistry*. The Pedagogical University Publishing House, HaNoi, Vietnam, 2015, 1077-1129

[4] Raymond E. Davis, Regina Fray, Mickey Sarquis, Jerry L. Sarquis. *Modern Chemistry*. Holt, Rinehart and Winston, United States of America, 2009, 710-745.

[5] Wolfgang Ponndorf (1926). "Der reversible Austausch der Oxydationsstufen zwischen Aldehyden oder Ketonen einerseits und primären oder sekundären Alkoholen anderseits". *Angewandte Chemie*. 39 (5): 138-143.

[6] William H. Brown. *Introduction to Organic Chemistry*. Saunders College Publishing, 1997, 587-589.

[7] Z. Wang, L. Zhu, F. Yin, Z. Su, Z. Li, C. Li (2012). Silver-Catalyzed Decarboxylative Chlorination of Aliphatic Carboxylic Acids, *J. Am. Chem. Soc.*, 2012, *134*, 4258-4263.

[8] Johnson, R. G.; Ingham, R. K. (1956). "The Degradation of Carboxylic Acid Salts by Means of Halogen - the Hunsdiecker Reaction". *Chem. Rev.* 56 (2): 219-269.

[9] Estelle Meislich, Herbert Meislich, Jacob Sharefkin. *500 Organic Chemistry Questions.* McGraw-Hill, America, 2013, 79-80.