

UNIVERSITY OF PORT HARCOURT

Chefs, Recipes and Kitchens

An Inaugural Lecture

By

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CChem FRSC, FCSN, FICCON

INAUGURAL LECTURE SERIES

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DEDICATION

This Lecture is dedicated to three Organic Chemists that have contributed enormously to my life:

- Late Christiana Mama Ngochindo
- Dame (Emereowa) Patience Ngochindo
- Lady Rhoda Ngochindo

ACKNOWLEDGEMENT

My culinary sojourn in Unique Uniport has ensured that this Lecture has been made a reality here by the unqualified cooperation I have received from members of staff of the Department of Pure and Industrial Chemistry which they had insisted I head, in spite of all protestations.

It was because Dr. D.J. Chadwick (former Director, Novartis Foundation) believed in me that he encouraged me to remain in Liverpool after Navy Captain A.P. Diets-Spiff had sent me there to pursue an ambition that eventually led to an honours degree in Chemistry. Dr. Chadwick introduced me to Heterocyclic Chemistry, for which I will always be thankful.

My eldest brother, Sir (Emer) Festus N. Ngochindo, (MPA, Harvard; *FNISM*; *FNIIM*) was my anchor in life after our mother left us while I was at the age of three. I salute his sacrifice over the years, and the support from Madam (his wife, and my titular mother) who fed me with chemicals that transformed me into the man that now stands before you.

My wife, Rosy, and the kids: Jima, Dosei, Ochure, Gorei and Anasei have been patient with me and supportive over the years.

My brothers, Rev'd Canon (Prof.) Cornelius B.M. Ngochindo (Radio Doctor of Diabetic Fame) and Chief Godfrey W. Ngochindo; my only sister, Mrs. Cecilia Chinwi; with other extended Akara Clan/family members and in-laws, have contributed their quota in various degrees in shaping my perception of cooking and synthesis.

I appreciate my colleagues and friends, especially Prof. I.O. Owate and Prof. N.E.S. Lale who encouraged me to move over to the only Unique University in Nigeria. My Bishop and

ArchBishop, His Grace, Most Rev'd Ignatius C.O. Kattey, J.P., Bishop (Dr.) Moses Kattey, Rev'd Olaka N. Olaka, G.O. Pastor (Dr.) Douiye Aganaba and a host of other Spiritual Leaders have proved faithful in upholding me over the years. The students have kept alive the culinary escapade and have been wonderful in keeping faith with the style of the strange Chef.

Above all, I remain most grateful to The Lord God Almighty and the cloud of witnesses He has left at my disposal. To Him be dominium and praise forever.

Think over the culinary verse below.

THINK BROTHER

raph ngochindo

You like vegetable
Because it's palatable;
He thinks it's miserable.
If he's your brother,
Why don't you bother?

Your use of money
Could cause an acrimony
And stain a testimony.
Don't ask him to step aside,
'Cause he may backslide.

You think a little wine
Will not make you a swine;
To you that may be fine.
But there's no gain,
In causing your brother pain.

May the Lord sow the seed
To meet your brother's need.
In a world of greed,
Love for one another
Glorifies the Father.

The Vice Chancellor
Past Vice Chancellors
Members of the Governing Council
Deputy Vice Chancellors
Principal Officers of the University
Provost, College of Health Sciences
Deans of Faculties
Distinguished Professors
Directors and Heads of Departments
Visiting Academics and Colleagues
Captains of Industries
Cherished Friends
Unique Students
Members of the Press
Distinguished Ladies and Gentlemen

1.0 INTRODUCTION

It is with great pleasure that I stand before you to celebrate this academic festival commonly referred to as *Inaugural Lecture*. The pleasure comes from the fact that the occasion provides me with the opportunity to tell my story my own way. I could not have this privilege in my lecture theatre because my employers have not paid me to go there to tell stories. This is done only when the exercise has added to the understanding of Organic Chemistry. As a preacher and teacher of the Gospel (Minister without Collars), I am restricted in the amount of Chemistry I can refer to in my presentations.

This is indeed an auspicious moment as we listen and participate in this festival on the eve of our 50th Independence Anniversary. What a sobering thought that we are 50. The Golden Jubilee is golden if Nigerians deem it so. The budget

for the celebration is not of concern here; rather, what is paramount is the level of achievement over the years. To any informed mind, the present state of education in this nation should be of interest. We should find out where we stand in the international community we refer to as University (a *Universe City*). The positioning of the tertiary level of education is expected to rub off on the society as the gown is taken to town.

More relevant is the fact that Mr. Vice Chancellor assumed office only a few months ago. This festival would also provide the opportunity to draw his attention to the shopping trolley from chemistry, science and the university. What good is the Recipe if there are no funds to purchase the items stipulated in the Recipe. Congratulations, Sir, on your assumption of duty. May we be reckoned as an excellent university during your tenure.

Today is significant in another respect. It marks the end of my twelfth year as a Professor, having been promoted to that exalted position with effect from 1st October 1998. The twelve intervening years have given me the opportunity to reflect on my contributions, or lack of it, as we advance towards the magical year 2020. On whether Nigeria will be among the first or last 20 countries by that year remains to be seen. A possibility for the former exists in the recommendations from this discourse. This Festival celebrates Recipes and not Menus. An Inaugural Lecture is often described as an Intellectual *Harvest*. It becomes relevant, then, to describe Recipes as a logical follow-up to a Harvest. Some other Colleagues may handle the aspect of Menus while others can delve into the next level: “The Taste of the Pudding is in the Eating.”

We have seen the progression of thought and the pains of a struggle to market a career in which our Leaders have been

uninterested in the last few years. We have lost our best brains to the attractive packages offered by Banks and Oil Firms. We complained about inadequate lecture space for the students, yet they kept sending us lists of wards that must be admitted. In the face of lack of space to rest their tired heads after copying notes they did not see because they were outside by the window while the lectures were going on, we crammed six into a room made for two with attendant hangers-on (popularly known as *Attachés*). These dehumanising conditions have become the lot of those expected to excel in character and learning. One quickly appreciates why the few that leave the shores of this nation end up as the best brains in their environments. Some of us lived in single hostel accommodations with wash-hand basins, mirrors and cupboards to ourselves. Where did we get the contraption we now bequeath to our *Leaders of Tomorrow*?

Mr. Vice Chancellor, Sir, permit me to wander into a home such as the beautiful ones provided on campus for members of staff; it is three bed-roomed. They are so beautiful that there is presently a long queue of members of staff waiting in the wings to move into them. There is the **Sitting Room** that houses the music centre, flat screen television and settee for the relaxation of both guests and occupants. Close to this is the **Guest Room** for visitors that have to spend the night. There is the biggest bedroom known as the **Procreation Room** (especially important when the house is home to humans other than the couple). Attached to this room and the sitting room are two sanitary discharge cubicles for environmental sanitation. These are labelled the **Decongestion Units**. A third room serves as the **Incubation Room** where little images of the major occupants are allowed to increase in stature, wisdom and complexity in a process referred to as *maturing*. At the end of the process, they relocate. Relocation is either by jumping

or being pushed out. Also attached to the Sitting Room is the **Sustainability Unit** where occupants are re-invigorated by the consumption of refined chemicals. Chemicals served here are mostly organic in nature. They include carbohydrates, proteins, vitamins and lipids (fats and oils). Leading from the Sustainability Unit is the **Organic Laboratory**, which in common parlance is referred to as the *kitchen*. A relatively smaller room is added somewhere in the house to serve as a silo or tank farm - the **Store**.

Several reactions occur in the kitchen. These include the conversion of organic polymers into simpler molecules that can be absorbed by the continuous extraction tubes that line the inwards of both visitors and occupants of the house. The major reaction that occurs in the Organic Laboratory is *hydrolysis*: the conversion of a more complex molecule to simpler ones with water by a process commonly referred to as *boiling*. Water employed could be pure or impure, depending on the level of awareness of the occupants of this beautiful house. By these reactions, and given good culinary training, vegetables are converted to edible materials without much loss in their vitamin contents. At elevated temperatures, the oven finds use in another process of cooking known as *baking*. Deep or shallow heating in fats or oils (depending on the capability of the Head Occupant and the level of awareness of the Deputy Head) may also be employed in a process referred to as *frying*. Both boiling and frying could occur in the same process.

All the reactions that take place in the *kitchen* are based on the careful addition and manipulation of chemicals. The procedure constitutes the *Recipe* for the reaction (also called *cooking*) and instructions on what and how to add the components required in the process are usually fully described. Some of the ingredients listed in the Recipe are expected to be prepared and

kept handy **before** the cooking commences. The person cooking, auspiciously referred to as *Chef*, ensures strict compliance with the Recipe. Disaster strikes when *copycats* attempt the cooking. The story has been told of a young woman who called the mother on phone from a temperate country to seek assistance on the preparation of a Nigerian dish known to be the favourite of her husband. The ingredients were already boiling when the call was made. The outcome of the cooking process is better imagined than described. How about the one who clapped her hands on her boiling mixture? This was because she used to see her mother do that while cooking. Apparently, the mother of this lass used baked material, which was usually broken into pieces in the palm before the addition. The lass saw the final process of the addition without knowing what had gone on before the “clap.” She did not realise that the action was the concluding part of the addition of a vital chemical: sodium chloride. Her honey could not be persuaded to eat the salt-less food.

A typical recipe follows:¹

“Chicken Wings Chasseur

1 kg chicken wings
Salt
Freshly ground pepper
Plain all purpose flour
50 g butter
2 tablespoons oil
1 clove garlic, crushed
1 small onion, chopped
6 spring onions, chopped
100 g mushrooms, finely sliced
1 tablespoon chopped parsley

½ teaspoon dried thyme
250 ml chicken stock
120 ml canned tomatoes, chopped
Chopped parsley to serve

Cut off and discard the tips from the chicken wings, use the tips to make the stock. Pat the wings dry with paper towels, sprinkle with salt and freshly ground pepper, and toss in the flour to coat.

Melt the butter and oil in a frying pan and sauté the wings, a few at a time, until browned. Transfer with a slotted spoon to a plate, keep warm. Add the mushrooms and cook for a further 2-3 minutes.

Add the remaining ingredients, reserving some parsley, and season with salt and pepper. Bring the mixture to the boil, return the chicken wings to the pan, and cover. Simmer for 20 minutes, or until the chicken is tender. Sprinkle with chopped parsley to serve.... *Serves 6.*”

What has been described above can be compared with an organic chemistry laboratory procedure:²

***“HYDROLYSIS OF A NATURAL OIL
(SAPONIFICATION)***

Place 5 cm³ of the oil provided in a 100 cm³ round-bottomed flask, add 20% aq. NaOH solution (20 cm³) and ethanol (20 cm³). Connect a reflux condenser and heat to boil under reflux for 40 min and pour into a beaker containing a saturated solution of sodium chloride (brine, 50 cm³). Cool the mixture to room temperature with stirring and filter the soap *in vacuo*, wash with ice-cold water and present.

Extract the filtrate with ethoxyethane (20 cm³ X 2), dry (MgSO₄), filter and evaporate solvent to obtain the triol.”

It is noticed that instructions are given on what and how materials are to be used in the procedure described, in a manner similar to the Recipe for cooking.

2.0 CHOICE OF TITLE

In the present context, a Chef uses a Recipe to prepare some palatable dish while a Chemist follows a Reaction Procedure in the laboratory. In other words, Reaction Procedure is to a Chemist what Recipe is to a Chef. The major variation is the location of the process: a laboratory for the Chemist and the kitchen for the Chef.

Vice Chancellor, Sir, permit me to exercise some licence as I show that most of what I had done in the chemistry laboratory in the last few decades can be likened to what most cooks do in their kitchens. May I dare to say that most of what is done in the kitchen can be classified as *organic chemistry*. To this end, may I recognise the untiring role of women who perform their reactions in the laboratory called the kitchen even when they had been sapped of energy on a tiring day. Imagine a woman pounding away at the carbohydrate with a baby strapped on her back, while the man relaxes (perhaps without a day's job) in the sitting room.

It should be pointed out at the onset that the Chef is gender insensitive. Females are not necessarily the best cooks. Men have been reported to have won in cooking competitions in which women participated. Some young bachelors have excelled in cooking, to the extent that they became a threat to potential suitors. There is still the existence of junk food for

those who prefer the easy way out to the rigours of kitchen chemistry.

Esteemed audience, standing before you is the *Chef*. The reaction procedures constitute the *Recipes*. The Laboratories in which the reactions were carried out are the *Kitchens*.

3.0 A CASUAL LOOK AT ORGANIC CHEMISTRY

Organic Chemistry is simply defined as the chemistry of the compounds of carbon. This definition has its limitation in the fact that not all carbon-containing compounds are organic. The common compound CO_2 contains carbon but it is inorganic. Most of the carbon-containing compounds that occur in nature are organic. Organic chemistry was, therefore, once defined as the chemistry of compounds that occur naturally. The term *organic* arose from this concept: natural systems were regarded as **organised** systems. Synthetical organic compounds exist that do not occur naturally, thus showing another limitation of this definition. For the purpose of our discourse, it may be sufficient to adopt the initial definition of chemistry of carbon compounds. What is clear, though, is that all organic compounds contain carbon although not all carbon-containing compounds are organic.

Carbon is a unique element in the periodic table that is capable of forming an apparently limitless number of compounds. The carbon atoms can form a variety of long chains and ring structures. The vast number of possible organic compounds might be frightening to the uninitiated mind. Organic chemists have simplified studies by classifying organic compounds. A study of representative members of a class could yield properties that can be extrapolated to other members of the class. Some of the classes of organic compounds are shown in

Table 1. The list is by no means exhaustive. The acyclic (non-cyclic) structures in Table 1 can have their ringed counterparts. Thus, we can have compounds that are cyclic alkanes. Those are known as cycloalkanes. Features of a class of organic molecule could be combined with those of another class to form a new class of organic compound. For example, a molecule that combines both a carboxylic acid function with an amine function is referred to as an amino acid.

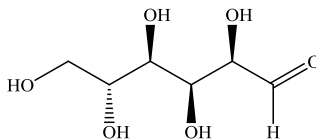
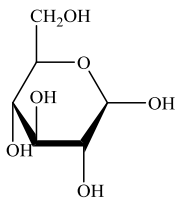
Table 1. Classes of Some Organic Compounds

S/N	Illustrative Structure	Class
1.	CH ₄	Alkane
2.	CH ₂ =CH ₂	Alkene
3.	CH≡CH	Alkyne
4.	CH ₃ Cl	Haloalkane
5.	CH ₃ OH	Alcohol
6.	CH ₃ SH	Thiol
7.	CH ₃ O CH ₃	Ether
8.	CH ₃ SCH ₃	Sulphide
9.	CH ₃ NH ₂	Amine
10.	CH ₃ CHO	Aldehyde
11.	CH ₃ COCH ₃	Ketone
12.	CH ₃ CO ₂ H	Carboxylic acid
13.	CH ₃ CO ₂ CH ₃	Carboxylic Ester

14.	CH_3CONH_2	Carboxamide
15.	$\text{CH}_3\text{CO-O-COCH}_3$	Anhydride
16.	CH_3COCl	Alkanoyl halide
17.	$\text{CH}_3\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$	Amino acid

The naming of organic compounds is a course on its own. For the purpose of our discourse, those that are mentioned here would be explained where necessary. There are rules that govern the naming of organic compounds. The International Union of Pure and Applied Chemistry (IUPAC) has given guidelines that aid in the naming of compounds to enhance easy identification and description. Even when some of these names may be unwieldy, they have the ability to assist in the identification of the compounds. They are similar to some of our Nigerian names. For example, Tamunotonye, Godspower, and Onyedikachi are descriptive, but written as one word. Similarly, 1,2-dichloroethane is written as one word.

Beyond the simple classification in Table 1 are some compounds of interest to the present Lecturer. These are known as heterocyclic compounds or heterocycles. Heterocycles are cyclic compounds in which one or more carbon atoms have been replaced with other atoms, especially oxygen, nitrogen or sulphur. Interest in heterocyclic compounds over the years has been largely due to their biological and pharmacological importance. For example, glucose, drawn in its cyclic structure as shown below, is a heterocyclic compound.



The variations possible in this grouping have increased the scope of study of heterocyclic chemistry to a level that several volumes now exist in the area. The ring sizes vary from single isolated three-membered compounds to large fused systems, many of which occur in nature. They could be fully saturated, partially saturated or fully unsaturated. Aromatic (with respect to electronic properties, not odour) heterocycles exist and are known as heteroaromatic compounds.



oxirane



thiirane



aziridine



oxetane



thietane



azetidine



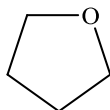
2H-oxete



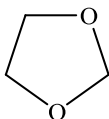
2H-thiete



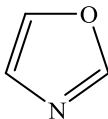
azete



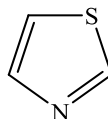
oxolane



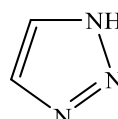
1,3-dioxolane



oxazole








thiazole



1H-1,2,3-triazole

For the heterocyclic compounds that would be encountered in this presentation, representative classes follow:

Table 2. Some Heterocyclic Compounds

S/N	Structure	Name
1.		Thiophene
2.		Furan
3.		Oxazoline
4.		Pyrrole
5.		Imidazole

4.0 LEVEL OF HOME ORGANIC CHEMISTRY

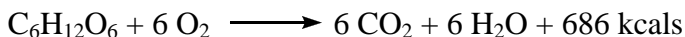
It may be of interest to know some of the organic chemicals we come across in the kitchen. On the breakfast table is margarine which contains biacetyl (butane-2,3-dione) as the major ingredient in its flavouring. Margarines are made by catalytic hydrogenation of oils to the consistency of butter, churning the product with skim milk, fortifying with vitamin A, and adding artificial colour and flavour. Fats (solids) and oils (liquids) are esters (called glycerides) formed from the

higher (C₁₂-C₂₂) fatty acids (straight, long chain monocarboxylic acids) and glycerol. In a more kitchen-like language, hydrogenation is the process of adding hydrogen atoms across the double bonds found in the fatty acids.

Fats differ from oils in the nature of their fatty acids. Fats contain a greater proportion of saturated fatty acids while oils contain more unsaturated fatty acids. Table 3 shows the various sources of common fatty acids.

Lipids are the main store of energy in animals. They provide insulation for vital organs, protecting them from mechanical shock and maintaining optimum body temperature. Unsaturated fatty acids are preferred over the saturated ones for health reasons; coronary thrombosis and paralytic strokes have been associated with the latter. Coconut rice may not be a healthy meal, after all.

Sugar is a carbohydrate known as sucrose and is composed of glucose and fructose units joined together. Bread is also a carbohydrate meal. Bread is made of starch flour. So are *garri* and *loiloi*. Carbohydrates are consumed in the form of starch and are the fuel of the body. Starch is a polymer of glucose units: amylose and amylopectin. Amylose molecules contain about 1,000 – 4,000 glucose units and constitute about 20 – 30 percent of most starches. Amylopectin, on the other hand, has more than 1,000,000 units of glucose. They are oxidised in the body to give energy, carbon dioxide and water by the equation:



The heat generated is the source of energy for the body.

Table 3. Common Sources of Some Fats and Oils

Source	Structure and Name	M.P (°C)
Coconut oil, Palm oil	$\text{CH}_3(\text{CH}_2)_{10}\text{CO}_2\text{H}$ Lauric acid	44
Coconut oil Palm oil	$\text{CH}_3(\text{CH}_2)_{12}\text{CO}_2\text{H}$ Myristic acid	54
Palm oil, Olive oil, Cottonseed oil	$\text{CH}_3(\text{CH}_2)_{14}\text{CO}_2\text{H}$ Palmitic acid	63
Olive oil	$\text{CH}_3(\text{CH}_2)_{16}\text{CO}_2\text{H}$ Stearic acid	70
Olive oil, Palm oil, Groundnut oil	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH})_7\text{CO}_2\text{H}$ Oleic acid	13
Linseed oil	$\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{H}$ Linoleic acid	-5

Proteins constitute a class of compounds essential to the existence of cells and are required to make amino acids needed by the body. They are giant polymers of amino acids, ranging in molecular weights from 6,000 for insulin to 41,000,000 for the protein portion of the tobacco mosaic virus. Each human has about five million different proteins performing functions beneficial to the individual. Eight of the amino acids required by humans must be ingested, as we are unable to synthesise them; they are the **essential** amino acids. About twenty other amino acids are joined in a variety of ways to form the proteins that are components of skin, hair, wool, feathers, nails, horns,

hoofs, muscles, tendons, connecting tissue and supporting tissue such as cartilage. Proteins are involved in communication (nerves), defence (antibodies), metabolic regulation (hormones), catalysis (enzymes) and oxygen transportation to cells (haemoglobin). Their primary function is bodybuilding and maintenance. The initial preparation in the kitchen results in irreversible **denaturation**. An example is the cooking of egg. Egg white is a colourless liquid containing albumins, which are soluble proteins. Heating causes the albumins to unfold and precipitate with the resultant formation of a white solid. Digestion begins in the stomach with its acidic environment, through the intestines until most of the amino acids end up in the liver. The liver processes both the digested amino acids and those made by the body to the cells. **Amino acids are organic molecules.**

All enzymes are proteins. For their biological activities, however, some enzymes need non-protein portions called **cofactors** which may be organic or inorganic in nature. When the cofactor is organic, it is called a **coenzyme**. Several coenzymes are directly related to **vitamins**. Some of these vitamins are organic compounds that cannot be synthesised by an organism but must be present in small amounts in the diet. Examples are thiamine (B₁), riboflavin (B₂), pyridoxine (B₆), ascorbic acid (C), folic acid (F) and nicotinamide. The special care taken in processing vegetables in order to preserve their vitamin contents is an exercise in organic chemistry. As we relish the taste of carrots, it should be remembered that carotene is the natural organic compound being enjoyed.

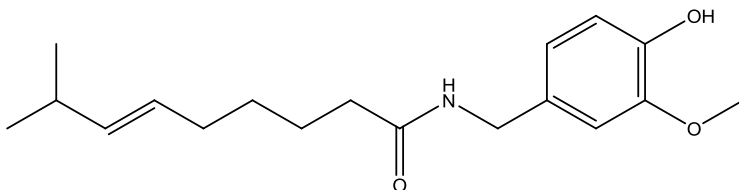
Some of the flavours used in the kitchen are organic compounds. They are listed in Table 4. It may become necessary to know, for example, whether the delicacy on the table has been prepared by a recipe that uses natural bananas or

synthetically butyl acetate (1-butyl ethanoate). For some, however, what matters is the taste and not the source.

Table 4. Flavours and Odours of Some Organic Compounds

Structure	Odour	Trivial Name
$\text{CH}_3\text{CO}_2(\text{CH}_2)_2\text{CH}_3$	Pears	Propyl acetate
$\text{CH}_3\text{CO}_2(\text{CH}_2)_3\text{CH}_3$	Bananas	Butyl acetate
$\text{CH}_3\text{CO}_2(\text{CH}_2)_4\text{CH}_3$	Pears	Amyl acetate
$\text{CH}_3(\text{CH}_2)_2\text{CO}_2(\text{CH}_2)_3\text{CH}_3$	Pineapple	Butyl butyrate
$\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$	Bananas	Isopentyl acetate
$\text{CH}_3\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$	rum	Isobutyl propionate
$\text{CH}_3(\text{CH}_2)_2\text{CO}_2\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$	Apples	Isopentyl valerate

Some other organic chemicals encountered in the kitchen include the **hot principle** in chilli, capsaicin (8-methyl-*N*-vanillyl-6-nonenamide) below.



5.0 ANOTHER LEVEL OF ORGANIC CHEMISTRY

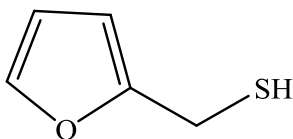
It has been demonstrated that organic chemistry is ubiquitous in the home. There are obvious limitations in performing reactions in the home. Elevated temperatures are limited to boiling water, steam distillation and frying with vegetable oils. Use of the microwave oven is a privilege a few enjoy. Use of hot plates is limited to those with electric cookers. Low temperatures are obtained with freezers and fridges. At best, lowest temperatures can be obtained by the mixture of ice/salt. Beyond all these limitations, facilities outside the kitchen setting need to be employed. This leads to the specialised organic chemistry laboratory.

At this higher level, organic chemistry is still defined as the chemistry of the compounds of carbon. Organic Chemistry has grown to be applicable in various spheres of life: drugs, explosives, dyes, fuels, plastics, fabricated fibres, glues, paints, etc. There are millions of organic compounds. Human existence is not possible without organic chemistry. The last meal taken before this discourse was organic. We drove in cars with organic tyres and tubes. Our dresses are organic, so are our shoes and hair wigs or modifications thereof. You hear me because of the electricity generated with organic compounds. There is virtually no part of human life which organic chemistry has not affected. No technological advance would have been possible without organic chemistry. ORGANIC CHEMISTRY, INDEED, RULES THE WORLD!

Vice Chancellor, Sir, it remains to show my role in this all encompassing subject area that has given birth to specialised areas such as:

Carbohydrate Chemistry
Heterocyclic Chemistry
Petroleum Chemistry
Alkaloid Chemistry
Protein Chemistry
Food Chemistry
Polymer Chemistry
Medicinal Chemistry
Agricultural Chemistry
Pharmaceutical Chemistry
Biological Chemistry (Biochemistry)

Heterocyclic chemistry presents a number of organic compounds ranging from the good (such as the DNA bases, the bad (such as nicotine from cigarettes) to the deadly (such as strychnine, a powerful poison). Cocaine, for example, is a habituating stimulant and pain reliever. It is an alkaloid. A molecule trivially known as furfuryl mercaptan has been found to be an essential constituent of natural coffee aroma



furfuryl mercaptan

6.0 STORIES FROM THE KITCHENS

6.1 Partly Liverpudlian

Liverpool, a city on Merseyside, North West England, is remembered mostly as the home of the *Beatles* (1962 – 1970). Music was in the air. There were also two rival teams: Liverpool Football Club (The Reds) and Everton Football Club

(The Blues). I chose the musical aspect as it allowed me to develop my talents with lead and rhythm guitars on a do-it-yourself (DIY) basis. Somehow, the appellation *RINGO* (from **R I N**gochindo) became popular with some friends who knew that Ringo Starr was one of the members of the *Beatles*. Getting fanatical with football was likely to lead to excess secretion of organic compounds. This informed the selective association in the city and thus became *partly Liverpoolian*.

I beg to return to the kitchens. The first of these is the Robert Robinson Laboratories, Department of Organic Chemistry, University of Liverpool. The School of Chemistry in Liverpool had two departments during my years there (1976 – 1982): Department of Inorganic, Physical and Industrial Chemistry, and the Department of Organic Chemistry. This showed the importance attached to Organic Chemistry. By the time I returned on an academic visit in 1989, both departments had been merged for financial reasons.

6.2 Starting With a Regioselective Recipe

Furan, thiophene and *N*-substituted pyrroles undergo predominant electrophilic substitution at the 2-positions. This reactivity pattern makes the syntheses of the 3-substituted derivative a challenging problem. It is possible to discourage reactivity at the 2-position by the use of electron-withdrawing groups at one of the 2-positions. However, regioselectivity is often poor. Another method that works well for *N*-substituted pyrroles is the use of bulky substituents either at the 1-position or as part of the electrophile (electron deficient species). It is comparable to a very fat passenger on the front seat of a taxi. No matter the insistence of the driver to carry two passengers at the front, no other paying passenger would like to sit there.

Where the passenger is unable to pay for the two front seats, the driver may insist on rejecting the very fat passenger.

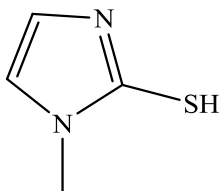
Lithiation (the exchange of hydrogen atom with lithium atom) occurs at the 2-position as well. This makes the position of substitution anionic (electron rich). An electrophile can then be introduced at that position. This allows for *regioselective* synthesis. What this means in kitchen terms is that the Chef decides where browning of the chicken should occur during roasting: top or bottom. The scrambling of substituents in the nucleus is, thus, avoided.

The use of a directing group at the 2-position of thiophene leads to metallation at the adjacent 3-position. It is like an usher directing people to their seats at a function. Application of this principle to furan and *N*-methylpyrrole led to regioselective metallation at the adjacent 3-positions. The metallation ratio of 3:5 was found to be 9.5:1, an improvement on 1.4:1 reported for thiophene. This methodology afforded new compounds that were fully characterised and published prior to my PhD defence.³ The directing group in this study played a dual role: in addition to its directing ability, it had a stabilising effect on the pyrrole ring that is known to be susceptible to acid-catalysed polymerisation.⁴

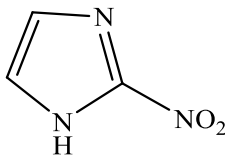
6.3 The Young Shall Grow

Another heterocycle of interest is the imidazole ring. This seemingly simple molecule with only two nitrogen atoms and three carbon atoms has proved fascinating over the years because of its natural occurrence, biological, pharmacological, catalytical and ligating properties.^{5,6} Some of these imidazoles with simple structures can be readily prepared from the parent imidazole while others may involve the construction of the

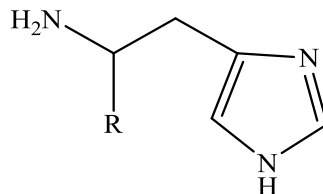
ring from acyclic precursors. Some of these simple imidazoles are shown below:



Methimazole

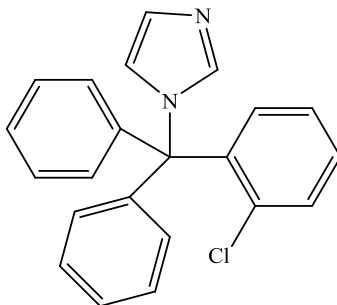


Azomycin



R = CO₂H Histidine

Methimazole is an anti-thyroid agent; azomycin is an anti-trichomonal agent; histidine is an amino acid and clotrimazole is an excellent fungicide used in the preparation of such creams as *Visita Plus* and *Funbact-A*.

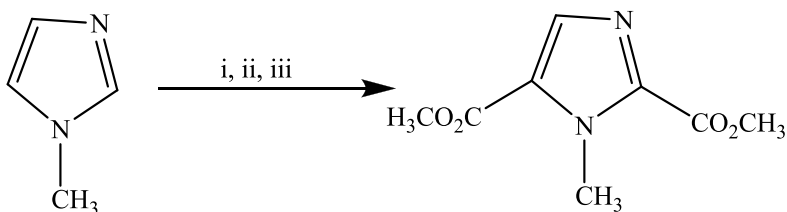


Clotrimazole

The reactions of the nucleus, however, are more complex. The site of electrophilic substitution depends on the nature of the electrophile and the reaction conditions, and substitution may occur at any one or all of the three nuclear carbon atoms. It has been established that the best route to the introduction of electrophiles is *via* lithiation.

When I was only three years old, probably in the year that my mother died, some workers published a paper on the monolithiation of *N*-substituted imidazole at the 5-position in 1.5% yield.⁷ This was considered a significant development as it provided 1,5-disubstituted imidazoles that were of choice in modelling. Another paper was later published by another set of workers in support of this finding of monolithiation at the 5-position.⁸ The beauty of science is that one's claims are open to scrutiny.

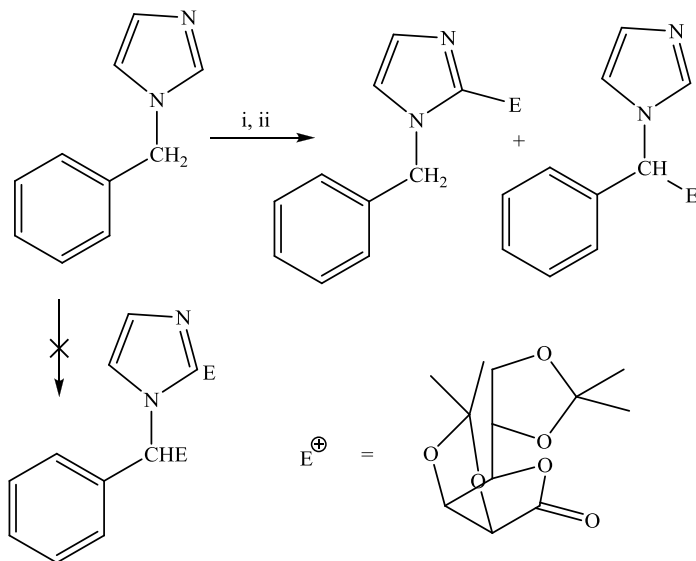
The conditions employed by the first researchers were repeated with careful transformation of the product to the methyl ester with ethereal diazomethane. We found some 23 years later that the report may be in error as we isolated the 2,5-disubstituted ester in 2.4% yield (Scheme 1). This suggests that the 2,5-dicarboxylic acid was formed, followed by 2-decarboxylation. The 2-carboxyl group had been established previously to be extremely labile.



Scheme 1. Reagents: i, BuLi; ii, CO₂, H₃O[⊕]; iii, CH₂N₂

With regard to the second report of 5-monolithiation with 2 mole equivalent of the lithiating agent, we are of the opinion that what actually happened was sequential 2-lithiation, followed by benzylic lithiation. Work-up with the bulky carbohydrate-derived electrophile would give a mixture of the products in Scheme 2 as two moieties of the electrophile cannot be accommodated in the product for steric reasons. The

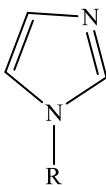
2- and benzylic substituted products must have been misinterpreted as the 2- and 5-substituted products. The yields of 30% and 12%, respectively, can be explained by steric reasoning.



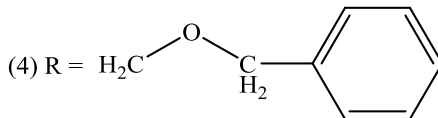
Scheme 2. Reagents: i, BuLi; ii, E[⊕]

We then went on to establish optimum conditions for both monolithiation and, for the first time, dilithiation of suitably substituted imidazoles.^{9,10} The merits and demerits of existing protecting groups used for monolithiation were examined for dilithiation. A **new** protecting group was then introduced for the 1-position of imidazole that allowed for both mono- and dilithiation.¹¹ Thereafter, three more protecting groups were introduced during a subsequent visit to Liverpool on a Fellowship sponsored by the Royal Society (a body directly funded by the British Parliament). It was a privilege to work with samples donated to my PhD Supervisor who had left Liverpool for Ciba Foundation (later Novartis Foundation), as

Director. More Protecting Groups were examined for both the 1- and 2-positions of the imidazole.^{12,13} Metallation reactions on the protected imidazoles (1) – (4) (Scheme 3) were studied. These studies pushed back the frontiers of science as several **new** compounds were synthesised and added to the lexicon of organic compounds after full characterisation.



- (1) $R = \text{SO}_2\text{N}(\text{CH}_3)_2$
 (2) $R = \text{CH}_2\text{O}(\text{CH}_2)_2\text{OCH}_3$
 (3) $R = \text{CH}_2\text{OC}(\text{CH}_3)_3$



Scheme 3.

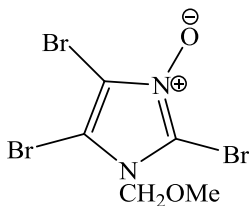
A Protecting Group in organic synthesis is a substituent that is introduced into a molecule to prevent a site from being attacked by the reagent in use. This substituent should be readily removable after the reaction or it becomes a Blocking Group. It is like a Chef who has a cut on a finger and needs to wash some bulbs of onions. The finger is plastered prior to the washing, and then the plaster removed after the washing.

The study of imidazole was taken a step further with the preliminary study of the decarboxylation of 1-alkoxycarbonylimidazole. This study questioned the reported mechanism in the literature as yields were improved upon and a more plausible mechanism postulated.¹⁴

6.4 All Things Work Together For Good

Another kitchen visited was The Ramage Laboratories, Department of Chemistry and Applied Chemistry, University of Salford, near Manchester in the U.K. The Royal Society sponsored this visit. Because it was for a period of one year, I sponsored my family (wife and four children) to taste of the fresh milk I had enjoyed while a student, from A/Levels in London to BSc and PhD in Liverpool. The greatest achievement in Salford was a review of work on the lithiation of imidazoles from the inception of studies in that area to December 1994.¹⁵ Several other attempts at regioselectivity were made but by another approach: metal halogen exchange.¹⁶ The period also afforded me the opportunity to work on my first text book.¹⁷ In spite of the overwhelming evidence for direct 2,5-dilithiation of imidazole, direct 2,4-dilithiation has been claimed.¹⁸ It has been shown that this is not possible.¹⁹ What could have been formed should be the 2,5-disubstituted product which undergoes 2-desilylation.

Accidents are known to occur in kitchens. Cooking gas explosion, fire outbreaks, burns from steam and hot oil, slipping over spilled water on tiled floors, etc., have been reported. In my case, Divine intervention prevented a disaster. The imidazolium *n*-oxide below was thought to hold the key to regioselectivity without the use of lithiating agents by the possible reversal of the order of exchange of the halogen atoms, analogous to pyridine *n*-oxides. 1-Methyl-2,4,5-triphenylimidazolium *n*-oxide had been prepared previously, but by cyclisation.^{20a}



All attempts to make the compound from 2,4,5-tribromo-1-methoxymethylimidazole failed. No reaction was observed with peroxytrifluoroacetic acid (from hydrogen peroxide and trifluoroacetic acid) as reagent after 10 hours of reaction at room temperature, boiling under reflux for 30 min. or extension of the heating to 20 hours. Starting material was also recovered even with a mixture of acetic acid, sulphuric acid and hydrogen peroxide as oxidant, and at a reaction temperature of 130 °C for 17 hours.

It was much later that it was discovered that the compound had been made by others and that it **exploded** in their hands. It remains to be imagined what would have happened if I had my way.

6.5 Kitchens Without The Kit

Vice Chancellor, Sir, permit me to use my licence of pun. The word *KITCHENS* can be split into **kit** and **chens**. *Chens* can be seen to be the plural form of *chen*, *i.e.* chen chen. *Chen Chen* in Eleme Language means something or someone that is inconsequential, purposeless, pointless and aimless. It is my position that Kitchens without the kit are useless (*chen chen*).

The Synthetic Organic Chemist is faced with a kitchen without a kit in this part of the world. This may take the form of Chemistry without Chemicals. Precursors for synthesis are not available. Solvents are not even available. Where there are

chemicals, how does one ascertain the purity and genuineness of the chemicals, given the penchant of our importers for adulterated goods? What if the label on the sample bottle was printed locally and sealed with appropriate standard sealant to deceive the consumer? Since routine analytical tools like infrared spectrophotometers (i.r.) and nuclear magnetic resonance spectrometers (n.m.r.) are not available, we cannot comment on samples purchased. Worse still, the products of reactions cannot be ascertained due to lack of i.r. and n.m.r. analyses. Microanalysis to confirm the molecular formula of a proposed structure is impossible. For some, the only way out is to mail samples to a foreign laboratory for analyses. This is only possible if one has a contact abroad.

How does one even perform reactions without power supply? There is no water supply to the laboratory for one to boil under reflux for several hours. One cannot create a vacuum with a water aspirator. Is there salvation in the October 2009 ASUU – FGN Agreement? Is synthetic organic chemistry possible in Nigeria? How many rotary evaporators are available in **all** the laboratories in a university combined?

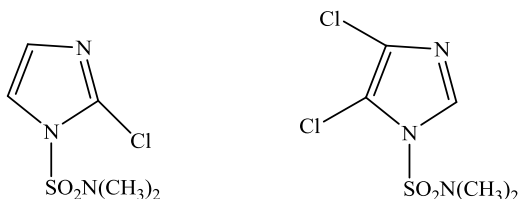
In spite of the picture above, some semblance of work continued at the home front.

7.0 WORKING UNDAUNTEDLY IN THE HOME KITCHEN

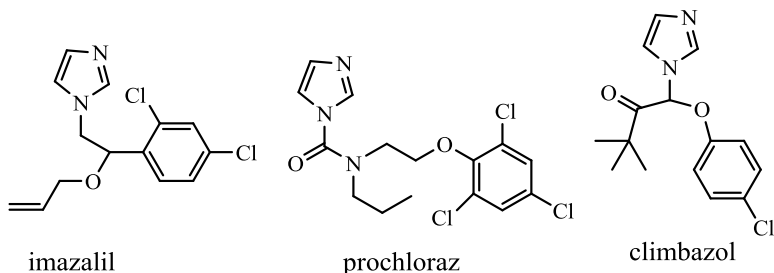
7.1 Applied Organic Chemistry

Some of the imidazole derivatives that were synthesised have been screened for biological activity.^{14,20b} The findings of some of these studies have been patented. After the initial discovery in 1985 of biological activity associated with *N,N*-

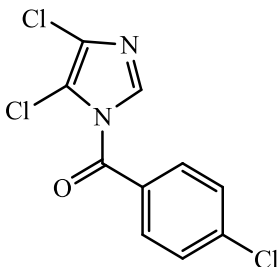
dimethylimidazole-1-sulphonamide [DIS, Structure (1), Scheme 3],²¹ activity was increased by introduction of chlorine atoms into the nucleus. The results from this study confirmed that the 2-chloro and 4,5-dichloro derivatives of DIS are fungicidal against *Aspergillus niger* and *Botryodiplodia theobromae*.²²



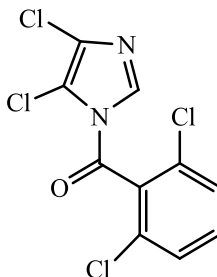
Some aryl-substituted imidazoles (such as imazalil, prochloraz and climbazol) have been reported to have fungicidal activity.^{5,6}



Two novel imidazoles with modified substitution patterns were synthesised and tested for activity. The new compounds, **jimazol** and **dosazol**, were found to be fungicidal against *A. niger* and *B. theobromae*.²³



jimazol



dosazol

1-Benzoylimidazole was chlorinated and the product studied. It was found to be fungicidal against fungi that attack tropical crops of economic importance: *Rhizopus stolonifer*, *Rhizoctonia solani*, *Aspergillus flavus*, *Sclerotium rolfsii* and *Fusarium solani*.²⁴

Consultancy work for Ministry of Agriculture, Port Harcourt, Imperial Chemical Industries Plc, Plant Protection Division, England and Rhône-Poulenc Agriculture Ltd., Essex, England focused on applied imidazole chemistry.²⁵⁻²⁷

In a recent study, the factors affecting the transesterification of palm triolein were examined as part of the work on Biodiesel.²⁸ Factorial design was achieved using two levels of three factors –duration of reaction, quantity of the alcohol in the reaction mixture and the quantity of catalyst with replications. Using regression analysis, the coefficients of the regression models were determined. The adequacy of the regression models was also determined. The optimum process conditions for the transesterification of palm triolein were investigated. The mathematical description of the process that guarantees maximum yields of the methyl and ethyl esters of palm triolein was derived. The effect of interaction between

the various factors was found to be relatively weaker than the effect of individual factors.

7.2 Other Productive Works

In addition to those reported earlier,^{2,17} another text, a novel, a book on drama, musical publication and a video script have been produced as part of productive work.²⁹⁻³⁴

7.3 Molecular Modelling

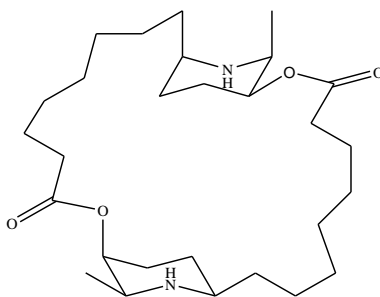
Models are representations, usually employed as projections of the real thing. Our beautiful accommodation mentioned earlier could be represented as a copy on a desk and in a form that could easily be appreciated. A model can be made of a car also. The model is a copy of the car, but is not a car. Models can also be made of molecules. These can show the number and arrangement of atoms in the molecule on a scale that reflects the essential features of the molecule.

The 1998 Nobel Chemistry Prize was awarded to People and Kohn for their work in Computational Chemistry and Molecular Modelling³⁵ while the 1999 Nobel Chemistry Prize was awarded to Ahmed Zewail³⁶ for his work in developing spectroscopic methods for studying reactions and in particular transition states,³⁷ an essential aspect of molecular modelling. These awards underpin the interest in the use of molecular modelling in studies involving organic molecules. Molecular modelling methods are now standard tools by organic chemists for searching for, rationalising and predicting structure and reactivity of organic, bioorganic and organometallic molecules. For example, Quantum Mechanics/Molecular Mechanics (QM/MM) methods have been used in the study of anticancer drug – DNA interactions.³⁸ Molecular modelling can provide a better insight to previously known phenomena.³⁹

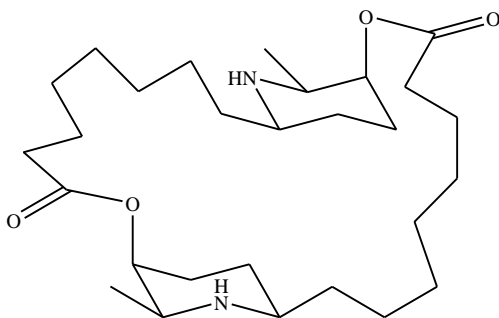
The present interest in molecular modelling arose more as a challenge than a conscious effort. The first study on *ab initio* parameters for an imidazole macrocycle⁴⁰ opened what may now be termed the floodgate to molecular modelling.

7.3.1 STRUCTURE OF CARPAINE. Paw paw (*Carica papaya*) is a fruit that is sometimes part of the recipe in kitchens, especially in the preparation of salads. It contains an organic compound known as **carpaine**, which belongs to the class of compounds referred to as **alkaloids**. These are naturally occurring amines found in plants. They are generally metabolites, many of which are physiologically active. Carpaine occurs in the seeds and green parts of the plant.

During one of the visits to Liverpool, I was discouraged from further work on carpaine as I was informed that all that needed to be done on the structure of carpaine had been done. For one used to challenges, it was identified that no report existed about its conformational analysis showing the energetically preferred conformation. The absolute configurations about the chiral centres in each of the heterocycles are (2*S*)-, (3*S*)- and (6*R*)-. These agree with empirical data and the dimeric structure proposed for the compound.⁴¹⁻⁴³ Two possible conformations, (5) and (6), can be drawn for carpaine.



(5)



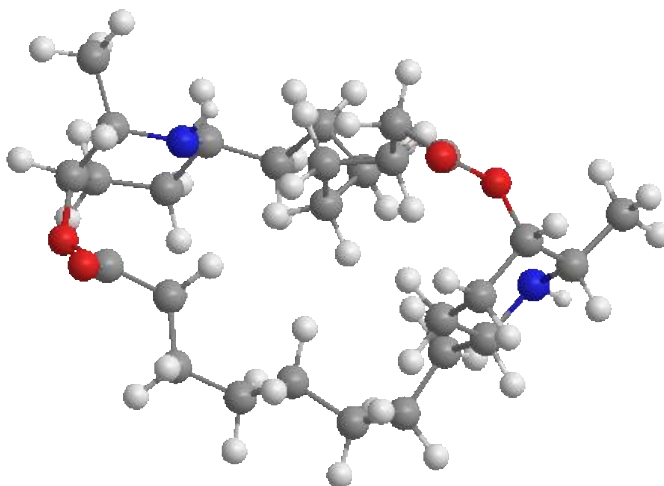
(6)

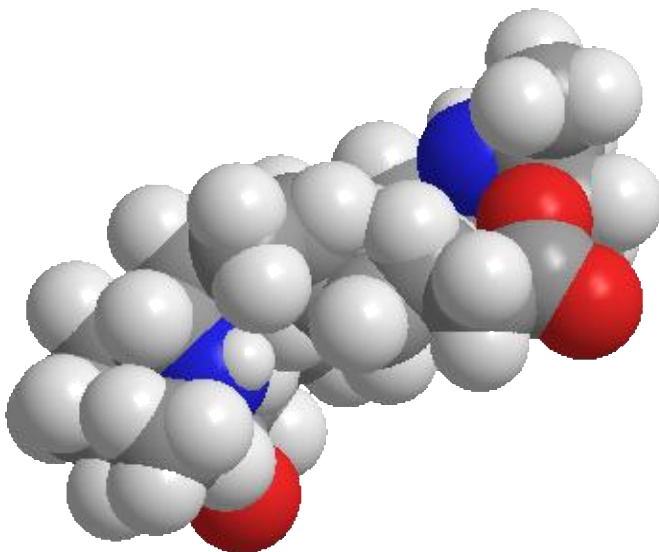
Molecular mechanical computations employing the MM2 force field was used to determine the preferred conformation. The MM2 method of molecular dynamics simulation uses Newton's equation of motion to simulate the movement of atoms. The atoms are treated as spheres and bonds as springs. The mathematics of bond deformation (Hooke's Law) is used to describe the ability of bonds to stretch, bend and twist. Non-bonded atoms (greater than two bonds apart) interact through van der Waals attraction, steric repulsion and electrostatic attraction and repulsion. This allows the conformational space accessible to a molecule to be explored. MM2 also serves to show Energy Minimisation for locating stable conformations. Single Point Energy Calculations are also available for comparing conformations of the same molecule, as in the case of carpaine. Combined with Quantum Mechanical Computations based on MOPAC (**M**olecular **O**rbita**P**ackage), the true structure of carpaine was established.⁴⁴ MOPAC uses approximations (to the Schrödinger's wave equation) in solving the matrix equations for a molecular system. The results of computation are given in Table 5.

Table 5. Properties Computed Directly on Structures (5) and (6)

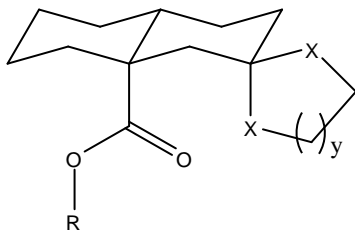
PROPERTY	(5)	(6)
Final Heat of Formation	18657.22872 KJ	2440.52693 KJ
Total Energy	-5387.92436 EV	-5555.99868 EV
Electronic Energy	-15700.78956 EV	-13812.68281 EV
Core-Core Repulsion	10312.86520 EV	8256.68414 EV
Ionization Potential	7.03866	7.94346

The more stable conformation is (6) with lower Total Energy. Thus, although the structure of carpaine had been postulated, there is now a mathematical justification for the structure assigned to it. The models are shown below as ball and stick, and as space filling models, respectively.





7.3.2 MODELLING OF *trans*-DECALIN ESTERS. For those interested in Natural Product Chemistry, the presence of the carbonyl group in a molecule is easily identified in the infrared (i.r.) region of the electromagnetic spectrum. The presence of two or more carbonyl bands in the i.r., however, does not imply the presence of more than one carbonyl group. It has been observed that a single molecule could show splitting of the carbonyl band. Factors responsible for the observed splitting have been identified to include Fermi resonance, intermolecular interactions and rotational isomerism.^{45,46} Band doubling in the decalin esters below has been attributed to rotational isomerism.⁴⁶ The carbonyl absorption in each of Structures (7) – (12) appears as a doublet in the i.r.⁴⁶ Insight to the origin of the doublet came from Molecular Modelling.



- (7) R = CH₃, X = O, y = 2
- (8) R = CH₂CH₃, X = O, y = 2
- (9) R = CH₂CH₃, X = O, y = 1
- (10) R = CH₂CH₃, X = S, y = 1
- (11) R = CH₃, X = S, y = 1
- (12) R = C(CH₃)₃, X = S, y = 1

The Dihedral Driver was employed to determine the energies of conformational variations. This enables the mapping of the conformational space of a model by varying one or two dihedral angles. A dihedral is defined by four contiguous atoms. The dihedral is rotated in increments of 5° through 360°. This results in the calculation of the energies of a total of 72 conformations for the molecule. The conformation of the model at any given point is viewed against a specific degree of rotation or energy setting, enabling the determination of the structural conformations of possible rotamers (rotational isomers) and their associated energies. Each isomer is a local minimum on the energy surface called the **potential energy surface**.

Dihedral rotation was performed about the bond that links the ester moiety to the decalin moiety; this rotates the ester while the decalin portion is stationary. A plot of the energy against the angle of rotation for each molecule shows two minima, which are taken to represent the rotamers that give rise to the carbonyl doublet observed in the i.r. spectra as shown in Figure 1.

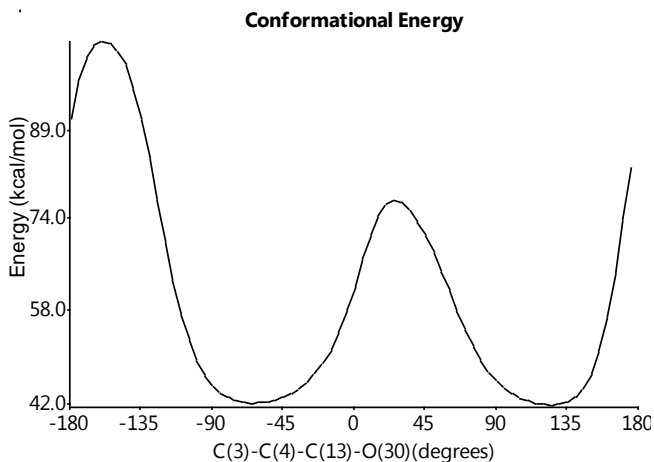


Figure 1. Conformational Energy of Structure (7)

The rotamers with energies at -65° and 125° have energies of 42.02 kcal/mole and 41.65 kcal/mole, respectively, and are shown in Figure 2.

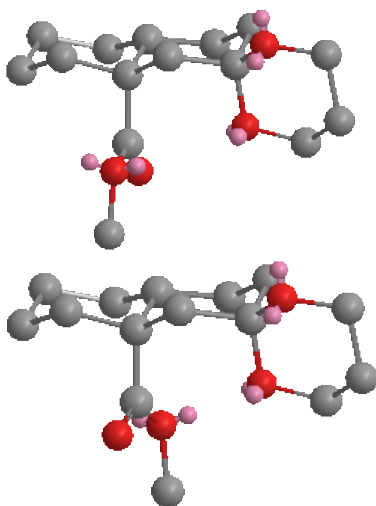
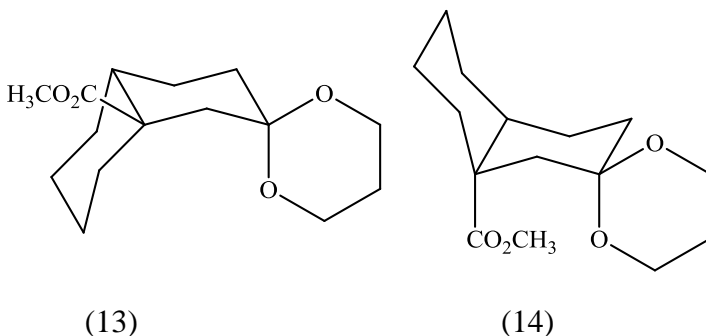


Figure 2. Rotamers of Structure (7)

Similar results were obtained for Structures (8) – (12). There is now a mathematical treatment to confirm the observed doublet.

7.3.3 MODELLING OF *cis*-DECALIN ESTERS. Results obtained from the *trans*-decalin esters have encouraged extrapolation to *cis*-decalin esters.⁴⁷ In this case, however, the orientations of the *cis*-decalins defer; this could be as shown in Structures (13) and (14).



The model of Structure (13) shown below, after energy minimisation, gives the plot that follows.

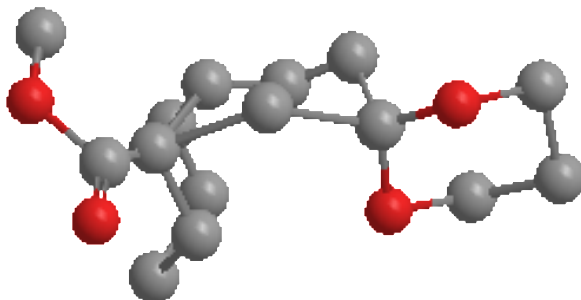


Figure 3. Model of Structure (13)

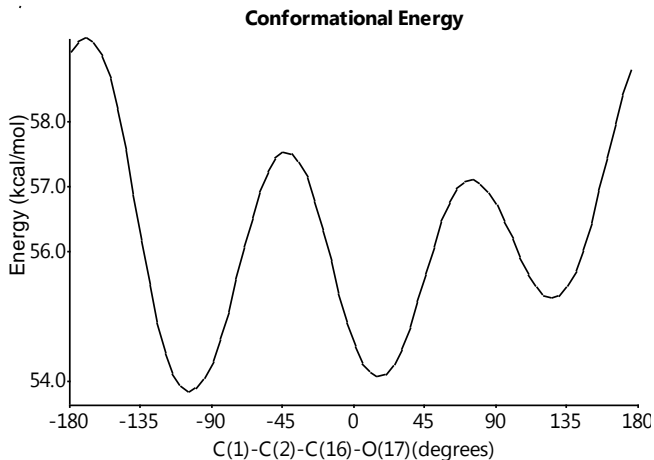
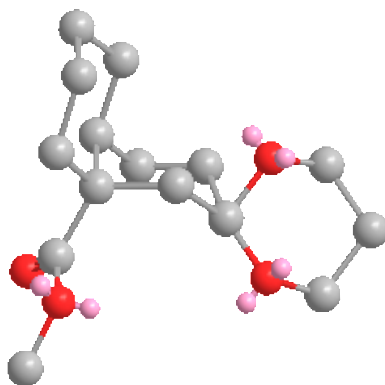


Figure 4. Conformational Energy of Structure (13)

The minima are associated with the rotation of the ester moiety in relation to the decalin ring. In Structure (14), on the other hand, rotation of the ester group is impeded by the ketal. The plot of the Conformational Energy is shown in Figure 6.



(14)

Figure 5. Model of Structure (14)

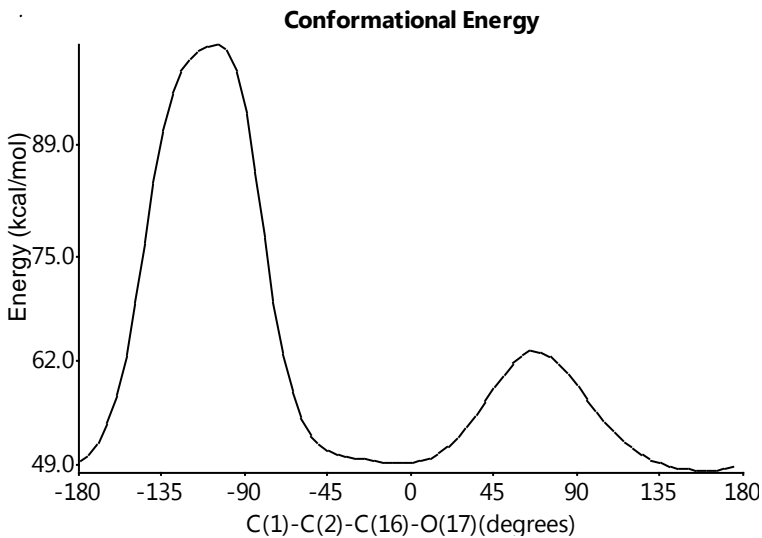
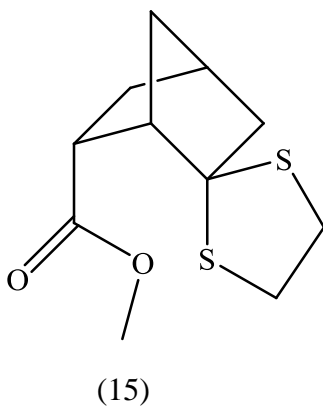


Figure 6. Conformational Energy of Structure (14)

7.3.4 MODELLING OF NORBORNANE ESTERS. A similar extension of the computational procedure to norbornane esters has been made.⁴⁸ Structure (15) shown as the model in Figure 7, has the Conformational Energy in Figure 8.



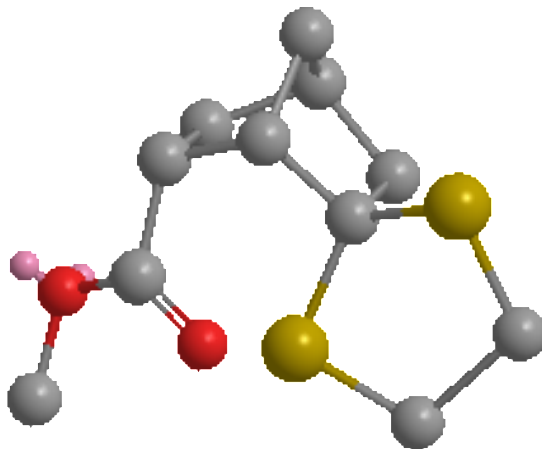


Figure 7. Model of Structure (15)

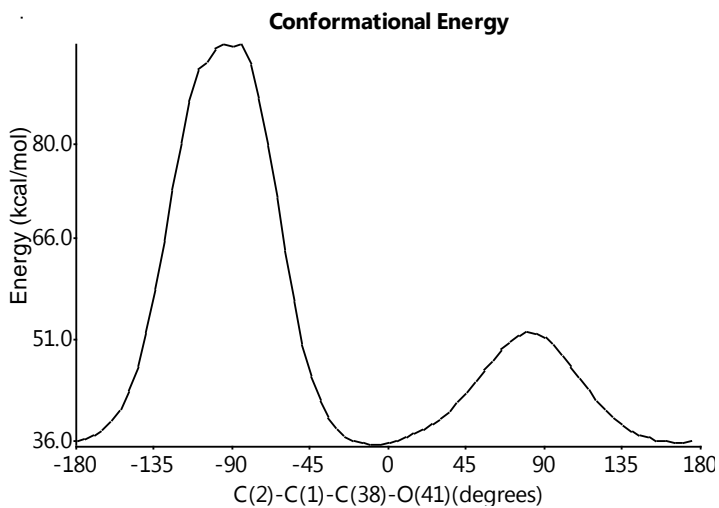


Figure 8. Conformational Energy of Structure (15)

8.0 BLOWING THE WHISTLE

Good housekeeping demands that the kitchen should be kept clean. No one waits for the first Saturday of the month for this exercise or we shall be co-habiting with cockroaches, rats and all manners of unwanted visitors. The problem is not so much the cleanliness of the kitchen but the way the wastes from the kitchen are treated. A good citizen uses the disposal facilities provided for the community, where one exists. In the absence of the provision of a disposal facility, then it is “doing what seems right in one’s eyes.” This has, unfortunately, led to one of the greatest problems faced by the human race – environmental pollution. Are chemists contributors?

8.1 Nigeria’s Giant Laboratory

Eleme has been recognised since the 1953 National Census to be one of the 250 ethnic nationalities in Nigeria. The people have their own language, culture, customs and peculiarities and occupy a land area of more than 300 square kilometres. Shell D’arcy started operations in Eleme in the 1950s. The Ebubu Oil Field, which comprises locations in the Eleme communities of Ebubu, Ogale and Onne, was discovered in October 1956. Crude Oil from Eleme was, thus, in the first shipment of 22,000 barrels from Nigeria in 1958.

Eleme has been described as Nigeria’s Giant Laboratory^{49,50} as it plays host to several major and important national and international establishments. These include:

1. Nigeria’s Premier Refinery at Alesa
2. Nigeria’ Fourth Refinery also at Alesa
3. Eleme Petrochemicals Complex (Indorama) covering parts of Akpajo, Aleto, and Agbonchia
4. Notore Chemical Industry (formerly, National Fertilizer Company, NAFCON) at Onne

5. The Federal Ocean Terminal at Onne
6. The Federal Lighter Terminal at Onne
7. The Oil and Gas Free Zone at Onne
8. Over 100 Oil Servicing Companies
9. The International Institute of Tropical Agriculture (IITA) at Onne
10. The Nigeria Naval College at Onne
11. The 4,000 Acres Equitorial Guinea Returnees Farm Project at Agbeta, Ebubu and Ogale
12. The Campus of the Rivers State University of Science and Technology at Onne
13. Oil Wells and Pipelines bearing crude oil and refined products.

As expected from all the chemical activities going on in the land, there has been a heavy environmental toll on the land and its people. Gas flaring, release of toxic fumes, pollution of ground water and disposal of wastes onto economically convenient sites at the detriment of inhabitants, are some of the prices being paid by the people for the release of their land for these facilities. The roads to the facilities are among the worst in Nigeria. Even the small stretch of road that leads from the Refinery Junction to the Refineries is in a state of disrepair. The East-West Road that heavy trucks ply from Onne is so bad that heavy-duty vehicles falling over and spilling their contents are common sights. The environmental assault on the people over the years has been borne with docility. Recent lessons should teach us that when there is no other alternative to moral reasoning by those that manage these chemical plants, resistance is encouraged. It makes economic sense to take care of the environment of the host community. The militant option is not the best.

Vice Chancellor, Sir, Chemists have been accused of environmental pollution. In the case of Eleme, the management of the facilities there is not in the hands of Chemists. Our colleagues in other professions determine the level of pollution or lack of it. The depletion of the ozone layer by carbon dioxide emission may also be readily cited. Several attempts have been made to stop gas flaring in Nigeria without success as at date. It is alleged at the same time that the cost of cooking gas is higher in Nigeria than in most countries that produce gas. Our kitchens would have benefitted from the use of clean gas rather than the soot of charcoal and firewood (and the attendant problem of deforestation). Our industries could run better should we supply them with gas, rather than flare the diminishing commodity. It is worst for the Giant Laboratory: the women crossing the roads with their bicycles loaded with firewood are knocked down by furiously driven escorted vehicles. For these women, gas in their homes would have given them more days to inhale the aerial pollutants and compete disadvantageously with the oil workers who go to the same market with them.

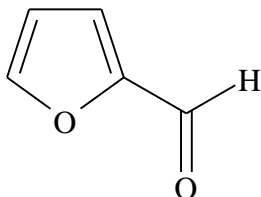
8.2 University Environment

An enlightened community such as ours should act as a pacesetter on issues of environmental protection. A conscious effort must be made in being environmentally friendly. Best practices thrown overboard by industries in search of huge profit margins cannot be ignored by the universities. That is why, Mr. Vice Chancellor, Sir, the laboratories (our kitchens) must be fitted with efficient and effective fume chambers. Some kitchens are known to have chimneys. These are not for Father Christmas only; they are to let out the fumes from the cooking vessels. Modern kitchens are fitted with extraction fans for the same purpose. Our members of staff, both

academic and technical, must be trained in the use of the various chemicals that we are exposed to, not only for themselves, but also for the sake of the university community. Environmental safety should be uppermost in our attitude to work.⁵¹

9.0 FROM WASTE TO WEALTH

While discussing the need for environmental friendliness, it may be noted that organic chemists show environmental concern by processing agricultural wastes to obtain useful chemicals. One of these is furan 2-carbaldehyde (16), trivially known as furfural.



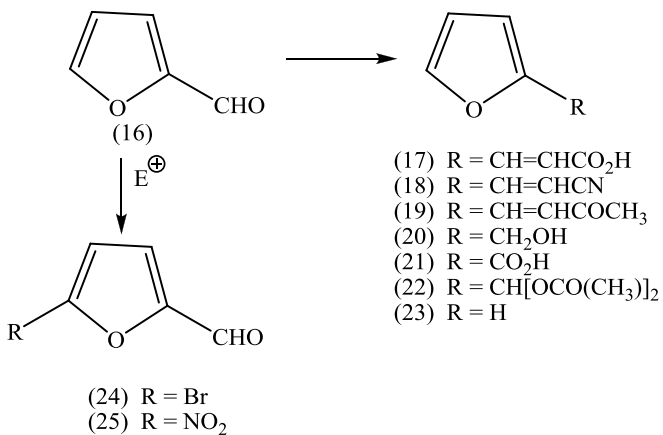
(16)

It was first isolated by Döbereiner as a by-product of methanoic acid synthesis from sugar substrates.⁵² It is obtainable in commercial quantities from pentosans found in renewable biomass residues such as corn cobs, husks from oat, cottonseed and rice, and sugar cane bagasse. The industrial development of the method of preparation is usually a factor of the type of raw material commonly available in a particular locality. Furfural contents of up to 23% in various vegetable wastes have been reported, with corn cobs among the highest.⁵³ The effects of concentration and nature of acid,

reaction time and particle size of biomass, on the yield of furfural have been reported.⁵⁴

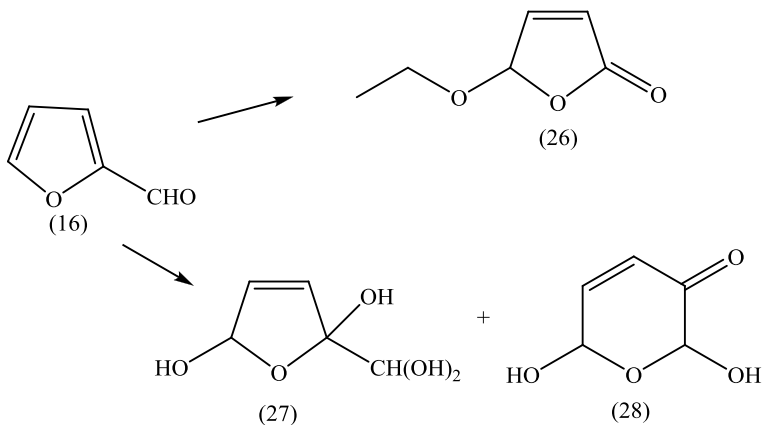
Furfural is a colourless liquid when pure, but darkens gradually with atmospheric exposure. Several of its physical parameters have been reported, including boiling point, melting point, density, refractive index and viscosity.⁵⁵ It provides low viscosity for resin formulation. It forms thermosetting resins with phenol. These have good physical strength and are resistant to corrosion, have high carbon yield, and are stable at elevated temperatures with less fire hazards. Organic concretes are insoluble, cross-linked, black resins, derived from furfural and propanone (acetone). The most important application of the chemical is in the petroleum industry where it is used as a selective solvent for separation of saturated from unsaturated compounds in petroleum refining. The compound also finds use in the vegetable oil industry in the differential solvation of saturated and unsaturated glycerides, in addition to its use in the paper and soap industries. A viscous copolymer of pyrrole and furfural is pyrolyzable to give high quality resinoid carbon fibres. These fibres are of lower density, greater mechanical strength and higher resistance to oxidation than ordinary graphite fibres.

The molecule undergoes several reactions typical of an aromatic carbaldehyde as in Scheme 4^{56,30}



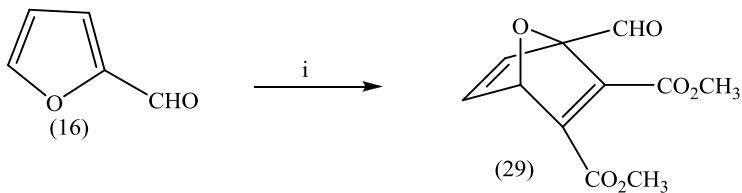
Scheme 4

It can be transformed to other heterocycles (Scheme 5)



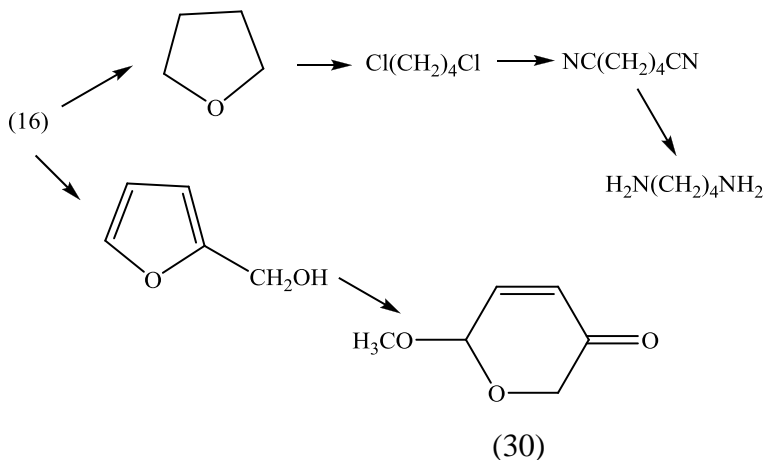
Scheme 5

It can also give cycloaddition adducts such as Structure (29) (Scheme 6).



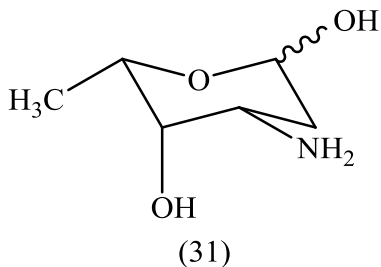
Scheme 6. Reagent: *i*, $\text{H}_3\text{CO}_2\text{C}-\text{C}\equiv\text{C}-\text{CO}_2\text{CH}_3$

Further transformations give the intermediate for the production of nylon, and sugar derivatives such as (30) (Scheme 7).



Scheme 7

The 2-methyl derivative of the pyranone has been used in the synthesis of Structure (31), DL-daunosamine. L-Daunosamine is the sugar component of adriamycin and daunomycin, anthracycline antibiotics effective as antitumor agents.^{57,58}

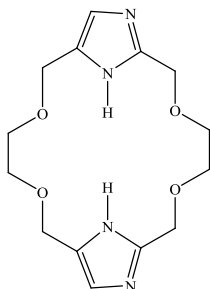


10.0 PROSPECTS

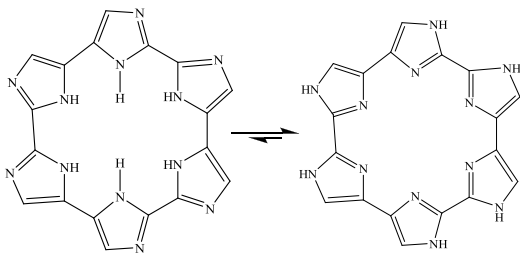
Vice Chancellor, Sir, when on Monday, 12 July 2010, you asked us to imagine the Uniport of tomorrow, some of us saw the possibilities in your Presentation. Still others went further to imagine what could be done, given the enabling facilities. There had been dreams. As long as these are not malaria-associated dreams, the possibilities are enormous. May I share some of these prospects for research in the kitchen.

10.1 Imidazole Macrocycles For Life

The challenge of incorporation of the imino nitrogen in the syntheses of imidazole macrocycles has been discussed.¹⁹ Such a macrocycle could allow for transfer of materials to and from within the macrocycle. A possible molecule that can effect such a transfer is exemplified by Structure (32).¹⁹ Still more promising would be Structure (33). This should be an aromatic macrocycle as six imidazole rings are linked directly (it should be noted that the imidazole ring is heteroaromatic).



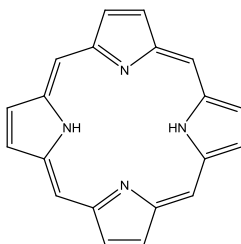
(32)



(33)

(34)

Structure (33) should also be tautomeric with Structure (34) by virtue of the ability of the azomethine and imino nitrogen atoms to exchange hydrogen atoms. The analogous structure to Structure (33) shown below is porphin, the simplest porphyrin.



Porphin

Porphyrins have a remarkable ability to form chelates with many metal ions with ease. They are highly coloured and are of great importance as they form the basic units of both the red blood pigment *haemoglobin* and the green leaf pigment *chlorophyll*. What can thus be achieved is replacement of the pyrrole-based natural macrocycle with an imidazole-based macrocycle.

10.2 Insulin

Insulin is a protein hormone consisting of two chains, **A** and **B** and is produced in the pancreas. It is essential for the regulation of carbohydrate metabolism. The model and structure of the A Chain are shown in Figure 9. The data generated from the structure are given in Figure 10. Many species have similar types of insulin, with differences mainly in amino acid units 8, 9 and 10 of the **A** chain as shown in Table 6.

Table 6. Variations in A Chain in Some Species

Species	Amino Acid Units of A Chain		
	8	9	10
Cow	Ala	Ser	Val
Sheep	Ala	Gly	Val
Horse	Thr	Gly	Ileu
Man	Thr	Ser	Ileu
Pig	Thr	Ser	Ileu
Whale	Thr	Ser	Ileu

Take away *CHEMIST* from *CHEMISTRY* and the result is *RY* (**R**otten **Y**olk) – raph ngochindo

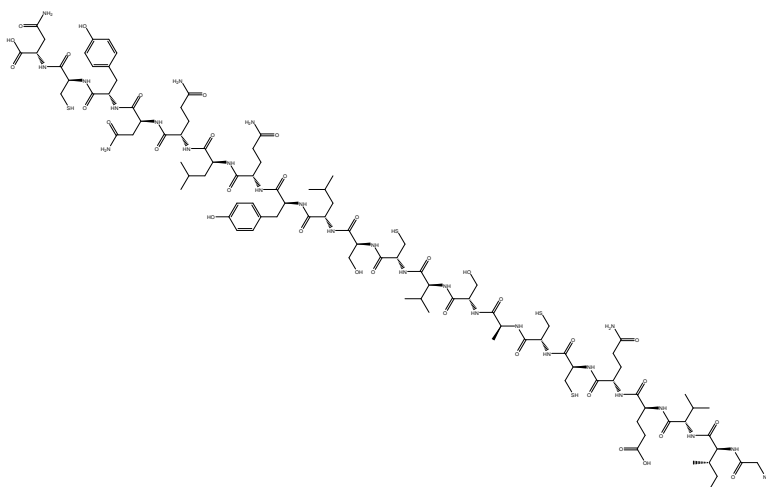
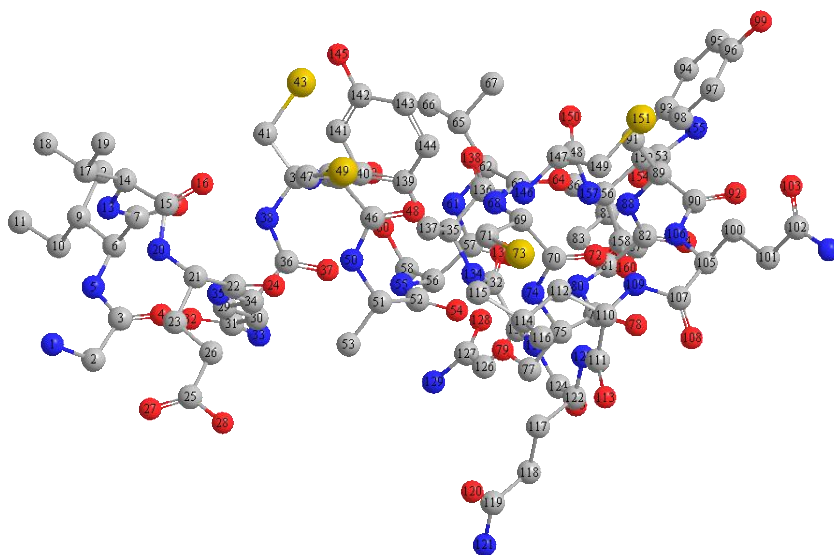


Figure 9. Model and Structure of A Chain of Insulin

Cartesian

Atom	X (Å)	Y (Å)	Z (Å)
N(1)	-10.9985	-2.9011	-0.7936
C(2)	-9.8174	-3.343	-1.545
C(3)	-9.0468	-2.1628	-2.0865
O(4)	-7.8591	-2.0524	-1.892
N(5)	-9.8203	-1.2516	-2.7541
C(6)	-9.2115	-0.0645	-3.3291
C(7)	-8.5634	0.7558	-2.2375
O(8)	-7.4065	1.0984	-2.3059
C(9)	-10.2348	0.7614	-4.1438

Internal Coordinates

Atom	Bond Atom	Bond Length (Å)	Angle Atom	Angle (Å)	2nd Angle Atom	2nd Angle (Å)	2nd Angle Type
C(3)							
C(2)	C(3)	1.51					
N(1)	C(2)	1.468	C(3)	111.031			
H(163)	C(2)	1.1137	N(1)	107.8549	C(3)	108.5216	Pro-R
H(164)	C(2)	1.1149	N(1)	109.7684	C(3)	111.3502	Pro-S
N(5)	C(3)	1.369	C(2)	113.9999	N(1)	-49.7146	Dihedral
O(4)	C(3)	1.2086	C(2)	121.007	N(5)	124.9604	Pro-S
C(6)	N(5)	1.4528	C(3)	120.0001	C(2)	179.9998	Dihedral
H(165)	N(5)	1.0191	C(3)	118.278	C(6)	121.6992	Pro-S

Measurement

Atoms	Actual (°/Å)	Optimal (°/Å)
C(158)-O(160)	1.338	1.338
C(148)-N(157)	1.369	1.369
C(136)-N(146)	1.369	1.369
C(132)-N(134)	1.369	1.369
C(124)-N(131)	1.369	1.369
C(111)-N(123)	1.369	1.369
C(107)-N(109)	1.369	1.369
C(90)-N(106)	1.369	1.369
C(82)-N(88)	1.369	1.369

Atom Property

Atom
N(1)
C(2)
C(3)
O(4)
N(5)
C(6)
C(7)
O(8)
C(9)

Figure 10. Data on A Chain of Insulin

The amino acid sequence for bovine insulin for the A and B chains are as shown below.

A Chain (21 amino acids):

HGlyIleValGluGlnCysCysAlaSerValCysSerLeuTyrGlnLeu
GlnAsnTyrCysAsnOH

B Chain (30 amino acids):

HPheValAsnGlnHisLeuCysGlySerHisLeuValGlnAlaLeuTyr
LeuValCysGlyGlnArgGlyPhePheTyrThrProLysAlaOH

The primary structure for bovine insulin shows three sulphide bonds between cysteine portions as follows:

A/Cys6-Cys11

A/Cys7-B/Cys7

A/Cys20-B/Cys19.

The A Chain has four cysteine molecules while the B Chain has two cysteine amino acids. Cleavage of the sulphide bonds leads to formation of thiols. Re-formation at the specified positions is a statistically daunting task. The primary structure is definitely deformed, as sulphide bond formation cannot be guaranteed to occur at the required cysteine molecules.

Before the advent of the fashion wig (in all its technicolour), some of my female Chefs recall the importance of the Permanent Wave (also called **Perm**). This is a series of waves or curls made in the hair by application of heat or chemicals, lasting several months. *Perming* of hair involves a process of cleavage and re-formation of sulphide bonds during setting. The new sulphide bonds formed determine the shape of the hairstyle. In the case of insulin, however, sulphide bonds are specific to certain cysteine molecules in the Chains.

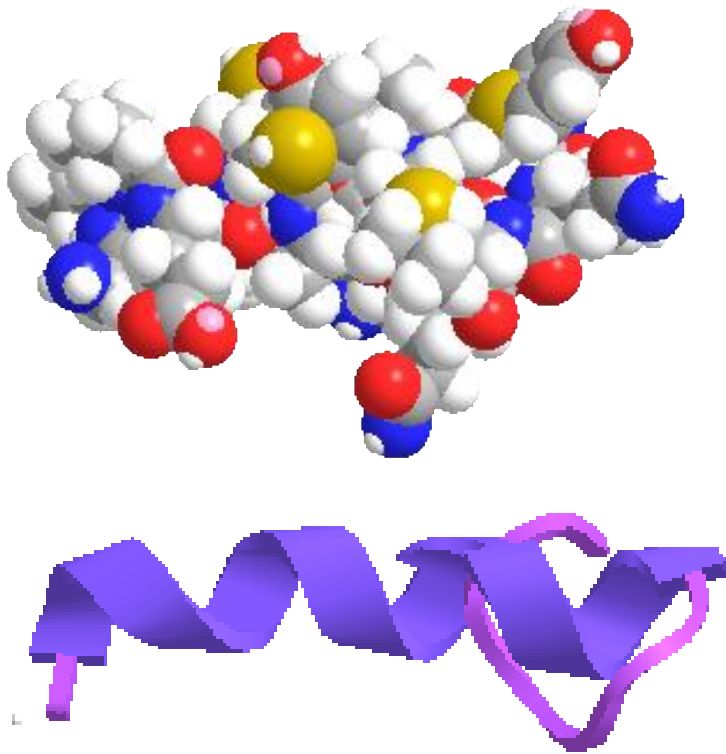


Figure 9. Space Filling and Cartoons Display Modes of A Chain of Insulin

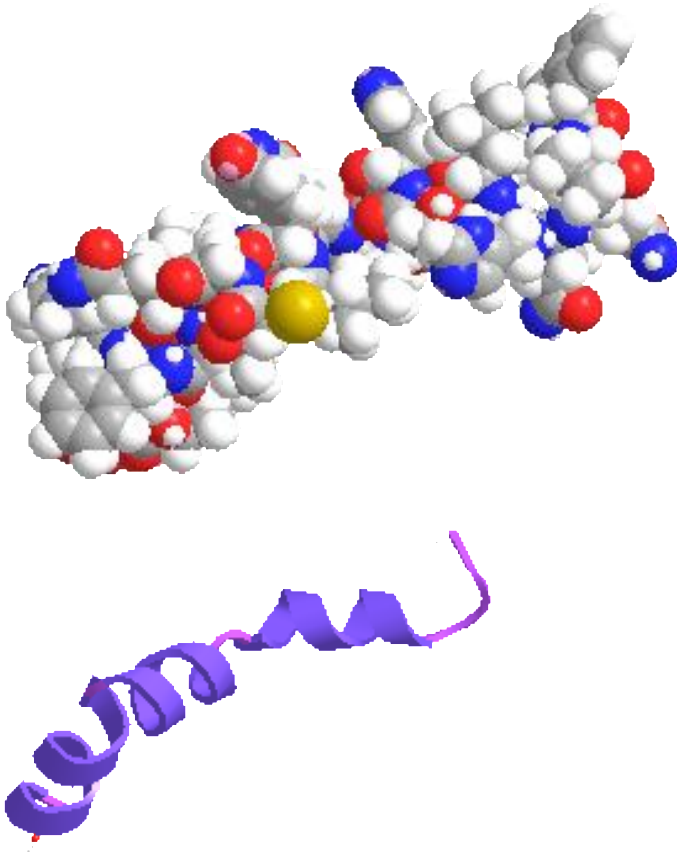


Figure 10. Space Filling and Cartoons Display Modes of B Chain of Insulin

Diabetics can often be treated with insulin from other species should they develop allergy to a particular type of insulin. In some cases, alteration of some amino acids in some proteins does not cause the protein to have an altered physiological effect. For insulin, the primary structure must be maintained for activity.

What may be explored is the use of nanotechnology to reform sulphide bonds at appropriate positions in damaged insulin. A nanotube is shown below.

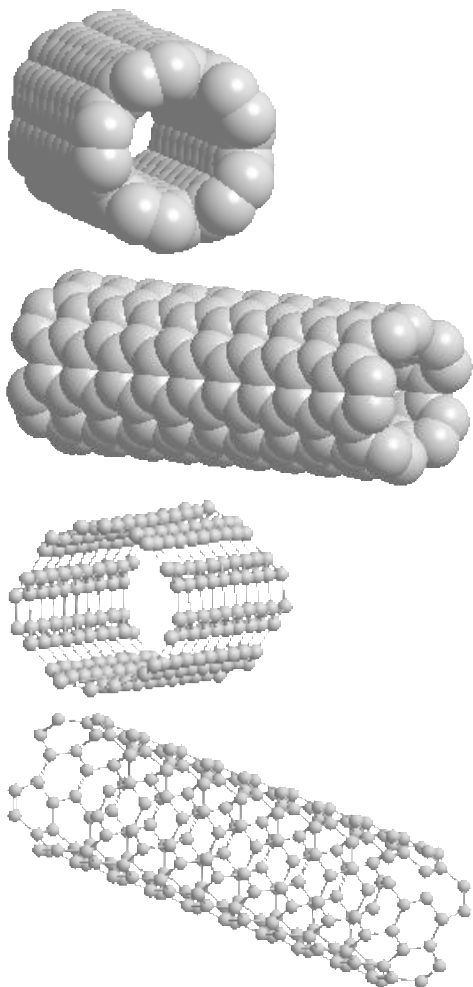


Figure 11. Space Filling and Ball and Stick Models of Nanotube(5,5)

This would allow the positioning of appropriate cysteine molecules such as to make for easy sulphide bond formation.

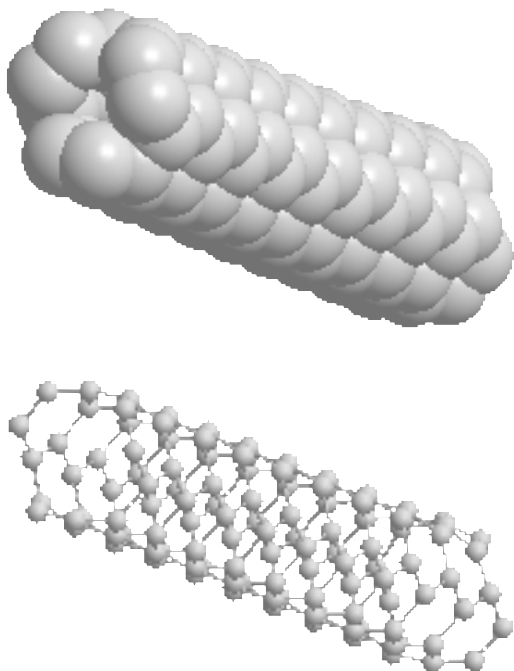
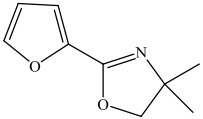
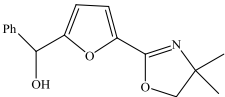
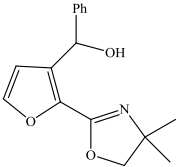
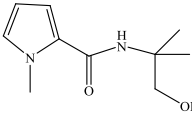
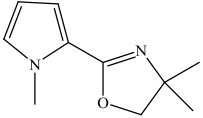
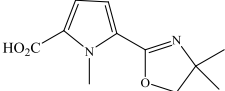


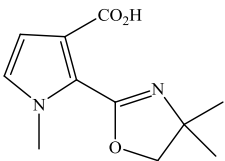
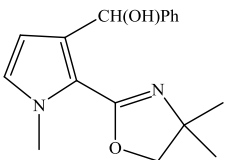
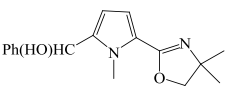
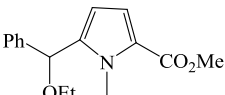
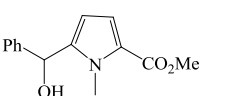
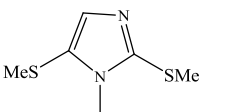
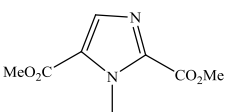
Figure 12. Space Filling and Ball and Stick Models of Nanotube(3,3)

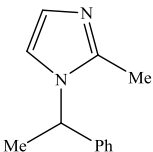
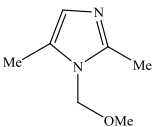
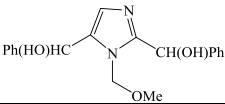
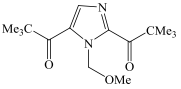
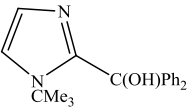
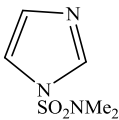
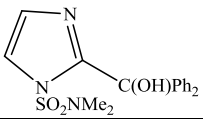
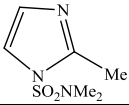
11.0 CONTRIBUTIONS TO THE RECIPE BOOK

The race is not to the swift. It is a privilege that the following compounds have been added to the lexicon of organic chemistry and assigned CAS Registry Numbers. Some others have been synthesized and patented, but without CAS Registry Numbers.

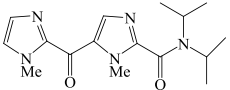
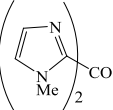
Table 7. Fully Characterized Compounds

S/ N	Structure	Name	Year
1.		4,4-Dimethyl-2-(2-furyl)oxazoline C ₉ H ₁₁ NO ₂	1982
2.		2-(5-Hydroxyphenylmethyl-2-furyl)- 4,4-dimethyloxazoline C ₁₆ H ₁₇ NO ₃	1982
3.		2-(3-Hydroxyphenylmethyl-2-furyl)- 4,4-dimethyloxazoline C ₁₆ H ₁₇ NO ₃	1982
4.		(1,1-Dimethyl-2-hydroxyethyl)- <i>N</i> - methylpyrrole-2-carboxamide C ₁₀ H ₁₆ N ₂ O ₂	1982
5.		4,4-Dimethyl-2-(<i>N</i> -methylpyrrol-2- yl)oxazoline C ₁₀ H ₁₄ N ₂ O	1982
6.		4,4-Dimethyl-2-(5-carboxyl- <i>N</i> - methylpyrrol-2-yl)oxazoline C ₁₁ H ₁₄ N ₂ O ₃	1982

7.		4,4-Dimethyl-2-(3-carboxyl- <i>N</i> -methylpyrrol-2-yl)oxazoline C ₁₁ H ₁₄ N ₂ O ₃	1982
8.		2-(3-Hydroxyphenylmethyl-1-methyl-2-pyrrolyl)-4,4-dimethyl-2-oxazoline C ₁₇ H ₂₀ N ₂ O ₂	1992
9.		2-(5-Hydroxyphenylmethyl-1-methyl-2-pyrrolyl)-4,4-dimethyl-2-oxazoline C ₁₇ H ₂₀ N ₂ O ₂	1992
10.		Methyl 5-ethoxyphenylmethyl-1-methylpyrrole-2-carboxylate C ₁₆ H ₁₉ NO ₃	1992
11.		Methyl 5-hydroxyphenylmethyl-1-methylpyrrole-2-carboxylate C ₁₄ H ₁₅ NO ₃	1992
12.		2,5-Bis(methylthio)-1-methylimidazole C ₆ H ₁₀ N ₂ S ₂	1983
13.		Methyl 1-methylimidazole-2,5-dicarboxylate C ₈ H ₁₀ N ₂ O ₄	1983

14.		2-Methyl-1-(1-phenylethyl)imidazole $C_{12}H_{14}N_2$	1984
15.		1-Methoxymethyl-2,5-dimethylimidazole $C_7H_{12}N_2O$	1984
16.		2,5-Bis[hydroxyl(phenyl)methyl]-1-methoxymethylimidazole $C_{19}H_{20}N_2O_3$	1984
17.		1-Methoxymethyl-2,5-bis(2,2-dimethylpropanoyl)imidazole $C_{15}H_{24}N_2O_3$	1984
18.		1- <i>t</i> -Butylimidazol-2-ylidiphenylmethanol $C_{20}H_{22}N_2O$	1984
19.		<i>N,N</i> -Dimethylimidazole-1-sulphonamide $C_5H_9N_3O_4$	1984
20.		2-Hydroxy(diphenyl)methyl- <i>N,N</i> -dimethylimidazole-1-sulphonamide $C_{18}H_{19}N_3SO_3$	1984
21.		<i>N,N</i> -dimethyl-2-methylimidazole-1-sulphonamide $C_6H_{11}N_3SO_2$	1984

22.		2-(2-Hydroxyethyl)- <i>N,N</i> -dimethylimidazole-1-sulphonamide C ₇ H ₁₃ N ₃ SO ₃	1984
23.		<i>N,N</i> -dimethyl-2,5-dimethylimidazole-1-sulphonamide C ₇ H ₁₃ N ₃ SO ₂	1984
24.		1-Methoxyethoxymethylimidazol-2-yl diphenylmethanol C ₂₀ H ₂₂ N ₂ O ₃	1990
25.		1-Benzyloxymethylimidazole-2-carbaldehyde C ₁₂ H ₁₂ N ₂ O ₂	1990
26.		2-(<i>t</i> -Butyldimethylsilyl)- <i>N,N</i> -dimethylimidazole-1-sulphonamide C ₁₁ H ₂₄ N ₃ O ₂ SSi	1990
27.		2-(<i>t</i> -Butyldimethylsilyl)-5-hydroxydiphenylmethyl- <i>N,N</i> -dimethylimidazole-1-sulphonamide C ₂₄ H ₃₃ N ₃ O ₃ SSi	1990
28.		1-Methyl- <i>N,N</i> -dimethylimidazole-2-carboxamide C ₇ H ₁₁ N ₃ O	1990
29.		5-Hydroxydiphenylmethyl-1-methyl- <i>N,N</i> -dimethylimidazole-2-carboxamide C ₂₀ H ₂₁ N ₃ O ₂	1990
30.		5-Chloro-1-methyl- <i>N,N</i> -dimethylimidazole-2-carboxamide C ₇ H ₁₀ ClN ₃ O	1990

31.		<i>N,N</i> -Di-isopropyl-1-methyl-5-(1-methylimidazol-2-ylcarbonyl)imidazole-2-carboxamide $C_{16}H_{23}N_5O_2$	1990
32.		Bis(1-methylimidazole-2-yl) ketone $C_9H_{10}N_4O$	1990

12.0 CONCLUSION

The ability of local Organic Chemists to meet the challenges of the 21st century is not in doubt. Access to journals and magazines published internationally ensures acquaintance with developments elsewhere in the world. The handicap remains the lack of facilities. World class research is possible at the University of Port Harcourt should research be supported. The following are recommendations.

1. The fume chambers attached to Ofrima, the home of science at the University of Port Harcourt, are in a state of disrepair. They need to be urgently repaired in order to put them to use to minimize environmental pollution.
2. Senate should resuscitate the provision of research grants to academics to cater for specialized research inputs, with special attention to the chemical sciences that require specialized chemicals.
3. There is an urgent need for a university-sponsored electricity supply to the Ofrima Building to ensure regular (even if not constant) availability of electricity in the building. Heating with kerosene stoves cannot be tolerated in an organic chemistry laboratory.

4. The Central University Laboratory should be stocked with infrared spectrophotometers, nuclear magnetic resonance spectrometers, gas/liquid chromatography/mass spectrometers and other analytical equipment. Investment in analytical equipment could generate income for the university.
5. The University Library requires funding to increase its capacity to provide up-to-date journals, with emphasis on subscription to e-Library facilities that guarantee access to e-journals. This would prevent “re-invention of the wheel.”
6. The younger academics need to be encouraged to pursue their studies to obtain their terminal degrees. Their current workload is a negation to their achievement of this goal.
7. Funding of tertiary education must be accorded priority by government in order to stem the drift towards mediocrity and to attract committed practitioners.
8. The regulatory body set up by government, the Institute of Chartered Chemists of Nigeria (ICCON), should be allowed to oversee both Chemists and Chemicals.

The Chef is not necessarily the originator of the Recipe or the architect of the Kitchen. Failure to follow the recipe religiously, however, is a failure on the part of the Chef. The environment in which the Chef operates cannot be viewed in isolation of the competence of the Chef to manage the surrounding. There would normally be clean-up in the kitchen to keep it neat and tidy. When the Chef slumbers or sleeps in the course of following a Recipe, the result may sometimes be what my children refer to as *Burnt Offering*.

Vice Chancellor, Sir, the Chefs on this side of the Niger Delta pledge commitment to the best practices of the profession. Our Kitchen shall be kept tidy and neat. We shall not bring dishonor to the Unique Gown when we go to Town. We shall

seek to place Unique Uniport among the best in the world.
Only provide the Kit for the Kitchen.

In a festival such as this, it is often difficult to satisfy the yearnings of all in the audience. For the attention you have shown, may I express my profound gratitude. Happy 50th Independence Anniversary Celebrations as you ensure that close attention is paid to the Recipe for the day.

THANK YOU

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UNIQUE UNIPOINT

Unique Uniport dares to look
Beneath the canopy of an open book;
Striding on the waves of life,
Founded in surroundings without strife.
Unique Uniport bares her gown
As her experts move to town
For Enlightenment and Self-reliance,
Projecting achievements with a radiance.

Unique Uniport has filled her slots
In learning, innovations and sports;
Takes character formation in its stride
Where excellence is her pride.
Unique Uniport seeks to impact
All those with whom she makes contact.
Generations acknowledge the processes
That fuel the uniqueness she possesses.

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