Organic processes of the future: technological implications

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Abstract The organic chemical industry of the future will be a function of two factors: (1) ever decreasing supplies of petroleum and natural gas and (2) maturity due to overcapacity and lack of new basic chemical technologies on a par with the petrochemical and polymer developments of the post World War II era.

Coal can replace petroleum and natural gas when necessary, an impressive technology having evolved in the past decade to make this possible. A tangible result is C_1 chemistry, which is now being used with petroleum-based synthesis gas and which will be used even more in the future (regardless of the source of the synthesis gas) for creative reactions, some of which are described in this paper.

To combat maturity much creative chemistry has evolved. Metathesis, the SHOP process, and sophisticated new polymers are some of the examples cited to provide an indication of the type of chemistry shaping the industry's future.

INTRODUCTION

To discuss the future in a field as complex as industrial organic chemistry can be an unrewarding exercise. Even so it is our obligation as scientists and technicians to try to understand that future, wrong though our understandings may be. It is more from our attempts to try to understand the future than from our success in predicting it that the future evolves. Thus we must not deny the process.

The future of industrial organic chemistry has both economic and technological implications. Dr Allen has already spoken about the former. This paper will concern itself with the latter.

THE ORGANIC CHEMICAL INDUSTRY AS A DISCIPLINE

The organic chemical industry that developed since World War II is 90 percent based on petroleum and natural gas. From these two key raw materials are obtained seven simple chemicals - ethylene, propylene, C_4 unsaturates, (butenes and butadiene), benzene, toluene, xylenes, and methane - from which the industry makes the bulk of its products.

From these seven compounds are made about 50 derivatives that account for about seventy five percent of the estimated 350 million tonnes of organic chemicals produced yearly, worldwide. There are, to be sure, about 30 thousand organic chemicals made industrially. But the broad picture against which the future is cast demands emphasis on these large tonnage materials. Incidentally, for teachers these simple statements provide insight into how to teach industrial organic chemistry. If a student knows where the seven basic chemicals come from and what the chemical reactions are that produce their 50 most important derivatives, he will have an understanding of his industry. Organised in this way industrial organic chemistry becomes a discipline.

THE DIMINISHING RAW MATERIAL SUPPLY

The future of the organic chemical industry is a function of many factors. Two of the most important are (a) the diminishing supply of petroleum and natural gas despite the present apparent "glut" and (b) its maturity due to overcapacity and lack of basic new chemical technologies on a par with areas such as petrochemicals and polymers.

One may tend to deemphasize the former point in today's economy, but there is no doubt that a finite supply of petroleum and natural gas will eventually force the chemical industry to shift its raw material base. This means that the seven basic raw materials must come from a source other than petroleum and natural gas. Let us consider this point first.

Coal is believed today to be the chemical industry's raw material of the future. As little as five years ago it was projected that by the year 2000 huge coal gasifiers would be making synthesis gas (carbon monoxide and hydrogen) for the chemical industry. From synthesis gas can be made the seven basic raw materials listed above, and accordingly the chemical industry could shift to coal. This concept is technically feasible but not entirely welcome one. Coal is a solid whose transportation is expensive. Plants to gasify it cost almost one billion dollars although the coal itself is cheap. Most important, coal is demeaning. If it is taken from the ground by human labour it demeans the human spirit. If it is obtained by strip mining it demeans the earth. Technology may solve these problems. Underground gasification, which has achieved some success, is a partial answer. Pollution is another basic problem associated with the use of coal. Nonetheless it could be used and probably will be. Olefins can be obtained from coal in several ways. One route is via the Fischer-Tropsch reaction in which carbon monoxide and hydrogen are converted over an iron catalyst to a petroleum-like mixture. This reaction provided the basis for the German military machine in World War II and today allows South Africa to be 75 percent independent of imported petroleum. From the Fischer-Tropsch reaction can be obtained aromatic and aliphatic compounds that can be converted to the seven basic raw materials. Indeed the reaction can be refined to provide olefins directly.

Fischer-Tropsch is not the only solution. Carbon monoxide and hydrogen can be converted to methyl alcohol which in turn can be cracked over a zeolite catalyst to olefins.

If we do not wish to use coal we can follow the example of Brazil of converting carbohydrate (in Brazil, sugar cane juice) to ethyl alcohol which in turn can be dehydrated to ethylene. The ethylene can be converted to propylene and 2-butene by chemistry now being commercialised by Arco and described later in this paper.

Aromatics can be derived from Fischer-Tropsch "petroleum" by catalytic reforming of a naphtha fraction, the process now used with petroleum naphtha. Also there is exciting chemistry in the wings that converts ethane, propane, butane, and even methane to aromatics using properly doped zeolite catalysts.

This chemistry emerged from work motivated by the belief 15 years ago that a petroleum shortage was imminent. An important result is the development of so-called C_1 chemistry, which allows the industry to do some remarkable things. Its importance is highlighted by the attention it is receiving at this meeting. C_1 chemistry is based on carbon monoxide, usually with hydrogen. The carbon monoxide, however, need not come from

coal. It may come from petroleum sources as indeed it has for the last four decades. There are two examples of C_1 chemistry that presage the future. The first, actually based on coal, is Eastman's ingenious process for making acetic anhydride. In the first step coal is gasified to CO and hydrogen. The plant is close to coal fields, eliminating the expense of coal transportation. A so-called Texaco gasifier has proved acceptable for the generation of chemical grade synthesis gas, which is converted to methanol. This is used to convert acetic acid to acetic anhydride. The methyl acetate is carbonylated in a homogenous chemical reaction to acetic anhydride:

$$CH_3COOCH_3 + CO \xrightarrow{cat.} (CH_3CO)_2O$$
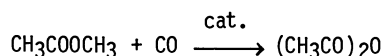
This reaction is noteworthy as an example of CO insertion. Also the fact that this chemistry is based on coal is impressive. Still another impressive factor is that the acetic anhydride is used in such a way as to eliminate the need for a plant to produce acetic acid. The acetic anhydride esterifies cellulose to make cellulose acetate, and in the esterification one mol of acetic acid results as a by-product. This is recycled to give one mol of methyl acetate for carbonylation. Conventional wisdom indicates that anhydrides are always made from two mols of acid. The Eastman chemistry does not violate this. One mol of acetic acid results as a by-product and the other mol is generated <u>in situ</u> by the carbonylation reaction.

Another example of C_1 chemistry has not yet been commercialised. Huge amounts of ethyl alcohol are produced in the United States today by fermentation under government subsidy. At the same time, methyl alcohol is cheap because its precursor, synthesis gas, is abundant because of the discovery of natural gas in numerous places in the world. By a reaction known as homologation methyl alcohol can be converted to ethyl alcohol:

$$CH_3OH + CO \xrightarrow{cat.} CH_3CH_2OH$$
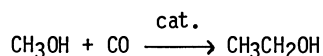
This may be done directly or it may be done via intermediate acetaldehyde which makes for greater selectivity of the desired product.

$$CH_3OH + CO + 1.5H_2 \xrightarrow{cat.} CH_3CHO + H_2O$$

$$CH_3CHO + H_2 \xrightarrow{cat.} CH_3CH_2OH$$
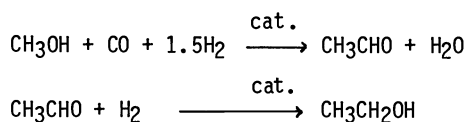
Economics are excellent when compared with either the subsidised or unsubsidised prices of fermentation ethyl alcohol in the United States. The original catalyst was dicobalt octacarbonyl. Subsequently about ten others have been shown to be effective. This reaction is an example of the power of C_1 chemistry whose development was motivated by a potential shortage of conventional raw materials. Since C_1 chemistry can be practiced with synthesis gas from petroleum as well as from coal, a new dimension, of which this reaction is typical, becomes available to influence the future of the chemical industry.

MATURITY

Maturity is the second factor that will influence the organic chemical industry of the future. Maturity means that there is in the world over- production capacity for chemicals, serious competition particularly for basic chemicals, and as a consequence reduced profitability.

One result is that very few new chemicals have been introduced in the past decade, and this trend will continue for the next few decades. There are two reasons for this. One is that in a mature industry, new materials are not needed to as great an extent as in a developing one. There are no new areas akin to the post World War II developments of petrochemicals and plastics to require new chemicals. The second is that federal regulations in the United States and other countries have made it difficult to introduce new chemicals. Only the pharmaceutical industry, and to a lesser extent the pesticide industry, are willing to make the investment that this requires. A pharmaceutical or a pesticide has a targeted use with a well defined market. Other chemicals normally require a tenuous process of development which may or may not lead to success. To make the investment in toxicity testing prior to undertaking expensive market development is something that most companies are not prepared to do.

But, to offset this, there are and will continue to be many new speciality polymers. Polymers do not require the rigid toxicity testing of monomeric chemicals because they are usually non-toxic. Also the developing aerospace and electronics industries have created markets, albeit small ones, for sophisticated polymers.

A second characteristic associated with the maturity of the chemical industry is, interestingly enough, creativity; but creavity within the frame of reference circumscribed by the existing chemical business.

A third characteristic that may be influenced by maturity is the concept of benefit-to-nations. Basically this means that large projects are undertaken by governments whose validity is not judged by the classical concept of profit and loss. Maturity is one of the reasons why the classical measure of profit and loss must be modified. Saudi Arabian petrochemicals is the best example. It can be shown that this venture is hardly profitable by conventional criteria. A large debt service consumes the margins. Yet Saudi Arabia considers the building of a technological base more important than profit in the capitalistic sense. Gasoline from methyl alcohol in New Zealand is another example as are Fischer-Tropsch chemistry in South Africa and subsidized fermentation ethyl alcohol in the United States:

Let us first discuss creativity as a function of maturity.

CREATIVITY

Creativity has been defined by great scientists such as Newton and Einstein as the reassembly of old knowledge with new insights and thus with the creation of new results. This is nowhere better illustrated than by the reaction of metathesis. Accordingly I should like to use metathesis as an example of the type of creativity that has influenced a mature chemical industry in the last five years and that will continue to do so in the future. Metathesis was invented at Phillips Petroleum in order to convert propylene, traditionally the cheapest of the olefins, into two more highly valued olefins, ethylene and butene:

$$2CH_2=CHCH_3 \xrightarrow{\text{cat.}} CH_2=CH_2 + CH_3CH=CHCH_3$$
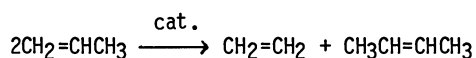
For a number of reasons Phillips never used this process after they invented it over twenty years ago. Meanwhile there is today a pending propylene shortage. To combat this

Arco, using Phillips technology, reversed the original objective and are converting ethylene and 2-butene into propylene. What is more the butene comes not from steam or catalytic cracking but from sophisticated chemistry using homogenous catalysis to dimerise ethylene:

$$2CH_2=CH_2 \xrightarrow{\text{cat.}} CH_3CH=CHCH_3$$

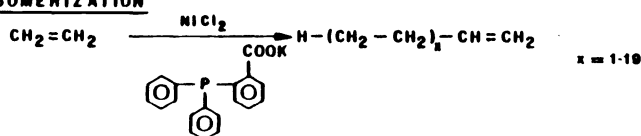$$CH_2=CH_2 + CH_3CH=CHCH_3 \xrightarrow{\text{cat.}} 2\ CH_3CH=CH_2$$
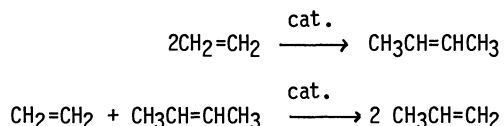
The metathesis reaction as originally invented demonstrates great ingenuity. Organic chemists have proclaimed it one of the most important organic reactions invented since World War II. The use of the reaction for exactly the opposite purpose for which it was originally intended demonstrates still another type of creativity.

The concept of metathesis has been extended further. One of the problems associated with the moulding of thermoplastic materials is high viscosity. This means that tremendous pressures are required to push large quantities of material into a mould and this limits the size of the moulding. One solution has been so-called Reaction Injected Moulding (RIM) in which low viscosity materials are placed in the mould and then allowed to react. The most used materials comprise an isocyanate and a polyol, which react quickly in the mould to provide a urethane. Hercules company devised a different concept based on metathesis. It was known that metathesis applied to a di-unsaturate with two non-congugated double bonds leads to a cross-linked polymer. Hercules chose the cheapest of all di-unsaturates, dicyclopentadiene. With a metathesis catalyst it forms a cross-linked polymer in the mould. This is another example of the extension of old knowledge to achieve a new result, a very important form of creativity, particularly in a mature industry.
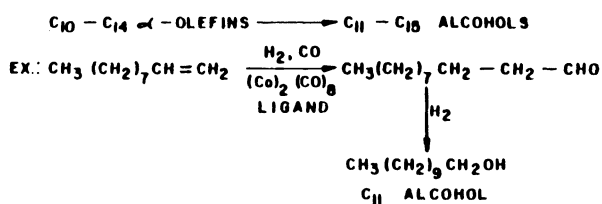
The most important example of creativity in industrial organic chemistry that has evolved in the last decade also uses metathesis. It is known as the Shell SHOP process. Shell took on the interesting objective of obtaining fatty alcohols with eleven to fifteen carbon atoms by ethylene oligomerisation . These are the preferred chain lengths for sulphation to alcohol sulphates for biodegradable surfactants. Nature provides C_{12} and C_{14} alcohols from coconut and palm kernel oils with, however, the less desirable lower and higher alcohols. Also the availability of natural products is subject to the vagaries of climate and sometimes the capriciousness of governments. Ziegler, of Ziegler-Natta catalyst fame, showed how to oligomerise ethylene to alcohols, but he obtained chain-lengths varying from C_4 to C_{24}. Shell decided to obtain only the desired chain lengths by a four step process shown in Figure 1. In this process almost every step was known. Thus, here is an example of a process that reassembled old knowledge to obtain a dramatic new result. In so doing, it provides an indication that the future, too, may be characterized by creativity.

The first step (Figure 1) involves oligomerisation, an old concept, although Shell invented a new process to provide alpha-olefins with chain lengths from C_4 to C_{40}. The key is a homogenous catalyst with an unusual ligand, which allows for oligomerisation but which because of its size inhibits chain growth to the polymer stage. From this mixture, the desired C_{12} and C_{14} alpha olefins are removed by distillation (step 2).

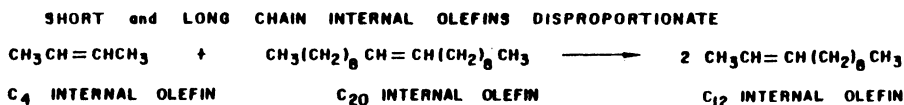## SHELL HIGHER OLEFINS PROCESS (SHOP)

1. OLIGOMERIZATION

$$CH_2=CH_2 \xrightarrow[\text{COOK}]{NiCl_2} H-(CH_2-CH_2)_x-CH=CH_2 \qquad x = 1\text{-}19$$

2. FRACTIONATION of α-OLEFINS

  a. $C_{10}-C_{14}$ α-OLEFINS

  b. C_4-C_8 α-OLEFINS

  c. $C_{16}-C_{40}$ α-OLEFINS

3. LINEAR HYDROFORMYLATION of $C_{10}-C_{14}$ α-OLEFINS

$C_{10}-C_{14}$ α-OLEFINS $\longrightarrow$ $C_{11}-C_{15}$ ALCOHOLS

EX.: $CH_3(CH_2)_7CH=CH_2 \xrightarrow[\substack{(Co)_2(CO)_8 \\ LIGAND}]{H_2, CO} CH_3(CH_2)_7 CH_2-CH_2-CHO$

$\downarrow H_2$

$CH_3(CH_2)_9 CH_2OH$

C_{11} ALCOHOL

4. ISOMERIZATION

  a. C_4-C_{10} α-OLEFINS $\longrightarrow$ C_4-C_{10} INTERNAL OLEFINS

  b. $C_{16}-C_{40}$ α-OLEFINS $\longrightarrow$ $C_{16}-C_{40}$ INTERNAL OLEFINS

EX: $CH_3CH_2CH=CH_2 \longrightarrow CH_3CH=CHCH_3$

$CH_3(CH_2)_{17}CH=CH_2 \longrightarrow CH_3(CH_2)_8CH=CH(CH_2)_8CH_3$

5. METATHESIS of C_4-C_8 and $C_{16}-C_{40}$ INTERNAL OLEFINS

SHORT and LONG CHAIN INTERNAL OLEFINS DISPROPORTIONATE

$CH_3CH=CHCH_3$ + $CH_3(CH_2)_8 CH=CH(CH_2)_8 CH_3 \longrightarrow 2\ CH_3CH=CH(CH_2)_8 CH_3$

C_4 INTERNAL OLEFIN C_{20} INTERNAL OLEFIN C_{12} INTERNAL OLEFIN

6. FRACTIONATION of INTERNAL OLEFINS

  a. $C_{10}-C_{14}$ INTERNAL OLEFINS

  b. C_4-C_8 INTERNAL OLEFINS

  c. $C_{16}-C_{40}$ INTERNAL OLEFINS

7. LINEAR HYDROFORMYLATION of $C_{10}-C_{14}$ INTERNAL OLEFINS

$CH_3(CH_2)_8 CH=CH-CH_3 \xrightarrow[\substack{(Co)_2(CO)_8 \\ LIGAND}]{H_2, CO} CH_3(CH_2)_8 CH_2-CH_2-CH_2-CHO \xrightarrow{H_2} CH_3(CH_2)_{11} CH_2OH$

C_{12} INTERNAL OLEFIN FROM
STEPS 5 AND 6 C_{12} ALCOHOL
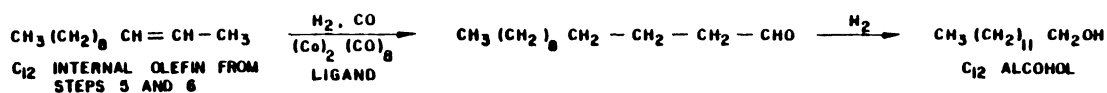
8. REPEAT STEPS 5, 6, AND 7 TO EXHAUSTION

Fig. 1 Shell higher olefins process (SHOP)

These are hydroformylated (step 3) by a process known as linear hydroformylation first used by Union Carbide to prepare normal butyraldehyde from propylene. The initial hydroformylation reaction led to a mixture of linear and branched products. Carbide and others found that the use of the Wilkinson catalyst, rhodium chloride and triphenyl phosphine, makes for a high degree of linearity. Shell used the concept (step 3) of linear hydroformylation, although not the same catalyst, to obtain C_{11} and C_{15} alcohols. The lower and higher alpha olefins (step 4) are combined and the double bond shifted to an internal position. Double bond isomerization is an old reaction well known in the literature and one which takes place readily, since the alpha olefin is the thermodynamically unstable isomer. In the next step, metathesis (step 5) is used to disproportionate these molecules and in a typical example, C_4 and a C_{20} olefins disproportionate to give two molecules of the C_{12} olefin. This example is idealised for the double bond need not be exactly in the middle position. After the metathesis reaction the desired C_{12}, C_{14} olefins are again obtained by distillation (step 6).

At this stage there is the problem of hydroformylation of a compound with an internal double bond (step 7). The answer is a catalyst, dicobalt octocarbonyl, with appropriate ligands, which causes double bond shifting to the terminal position. In simple terms the ligand is so large that it prevents the hydroformylation reaction from taking place at the internal double bonds. The double bonds have no choice but to shift to the end position to make the reaction possible.

Finally the compounds with undesirable chain lengths (step 8) are again circulated and again disproportionated so that more of the C_{12}-C_{14} molecules will form for removal by distillation and subsequent hydroformylation. The process is repeated to exhaustion.

This process, an excellent example of reassembly of old knowledge to achieve a new end result, has proved highly successful. It is to be hoped that it presages the creativity of the future chemical industry. There are other examples of creativity that serve as signals to presage the future, for undoubtedly this type of creativity will continue to combat and perhaps reverse the maturity of the chemical industry. However there are other concepts yet to discuss and one of these is benefit-to-nations.

BENEFIT TO NATIONS

There are today huge projects being developed that are not necessarily economic but that in one way or another benefit the nation that promulgates them. In the United States the production of fermentation alcohol is subsidised. Huge quantities are now being made for use in non-leaded gasoline. The result is that petrochemical alcohol is hardly economical and much capacity has been closed. This of course is bad for the petrochemical industry. It is doubtful that more energy is obtained from the fermentation alcohol than is consumed in its production and in the growth of its raw material. This uneconomical process, however, is supported because there is benefit to the farmers whom the government wishes to favour.

We see this in much more dramatic fashion in Saudi Arabia where so-called wellhead or associated gas, which is available at practically no cost, is being used for the production of chemicals. The net result of this is that chemical facilities in Japan and to a lesser extent in Western Europe have been shut down. Exports from Japan, Western

Europe, and the United States have been seriously inhibited and will decrease even more in the years to come. As a case in point, 80 percent of Japan's methyl alcohol is imported and there are only two indigenous suppliers left. In the United States and Western Europe methyl alcohol facilities have also been mothballed. It can be shown by conventional accounting that production of chemicals in Saudi Arabia is not economic. Even though the raw materials are cheap a tremendous debt has been incurred which must be serviced. There are freight costs and tariffs that contribute to making the production of chemicals in Saudi Arabia, using conventional profit and loss economics, uneconomical. This does not bother Saudi Arabia. They are going ahead full force because they believe there is benefit to their nation in developing a strong technological base.

Still another example is found in New Zealand where the so-called M-Gas process has been successfully developed. This process is based on a remarkable catalyst developed by Mobil, a zeolite known as ZSM-5. In this instance it dehydrates methyl alcohol to dimethyl ether,

$$2CH_3OH \xrightarrow{-H_2O} CH_3OCH_3$$
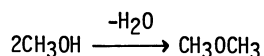
This dehydrates further to methylene radicals,

$$CH_3OCH_3 \xrightarrow{-H_2O} 2-CH_2-$$
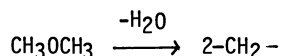
which rearrange to aliphatic and substituted aromatics molecules. The resulting combination is gasoline with a high octane number.

This development resulted from a natural gas discovery in New Zealand, which the government was eager to exploit. Thus it was decided to convert the natural gas to synthesis gas and then to methyl alcohol. New Zealand decided to use at least part of their methyl alcohol internally by converting it to gasoline. This is indeed dramatic chemistry. The plant in New Zeland has only recently been brought on-stream and is functioning satisfactorily. Is it, however, economical? Probably not by the conventional standards used to judge economic viability. It is, however, a benefit to New Zealand, not only because it provides New Zealand with an important technological base but also because it limits the import of oil that requires precious hard currency.

In the future, chemistry, much of it highly creative, will be used in large projects, mostly sponsored by governments, of the type just described. These will not necessarily yield a profit in the conventional sense, but they will in some way benefit the country that uses them.
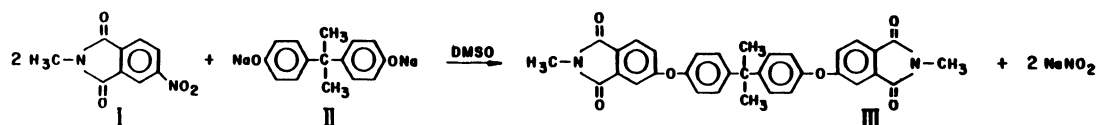
NEW POLYMERS

The point has already been made that maturity has led to a decrease in the introduction of new chemicals. Not so for sophisticated new polymers, some of which are essential to aerospace and electronic developments. These polymers make use of chemistry that the industry a few years ago would certainly have eschewed. Two examples will be cited to prove the point that modern polymer chemistry involves impressive creativity, hopefully of a type that will continue into the future.
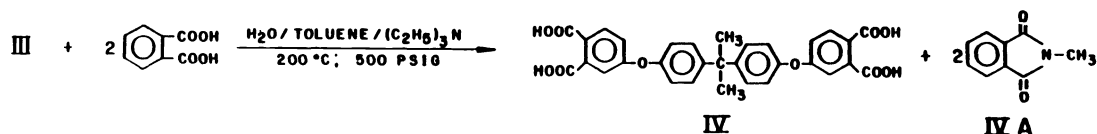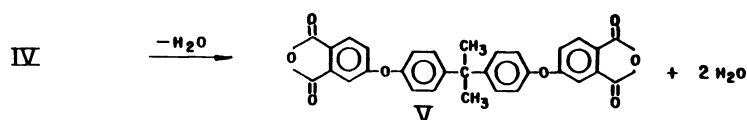
POLY(ETHER IMIDE) FORMATION

REACTION 1 (FORMATION OF BIS (ETHER SUBSTITUTED PHTHALIMIDE))

REACTION 2 (FORMATION OF BIS (ETHER PHTHALIC ACID))

REACTION 3 (FORMATION OF DIANHYDRIDE)

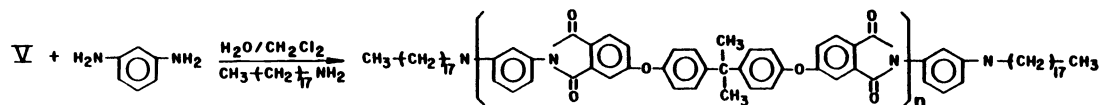### REACTION 4 (FORMATION OF POLY(ETHERIMIDE))

Fig. 2 Poly(ether imide) formation

Polyimides are polymers with good properties whose use is inhibited by intractibility. General Electric has in part solved the problem with a polymer that has imide linkages and accordingly some of the properties of a polyimide, but which is also thermoplastic. Their polymer is a poly-(ether imide) whose chemistry is shown in Figure 2. The first step is the reaction of the sodium salt of bisphenol A with 4- nitro-N-methylphthalimide. Interaction of the two materials in dimethyl sulphoxide leads to a nucleophilic displacement (a reaction previously unknown in industrial organic chemistry) to provide sodium nitrite and a molecule in which the bisphenol A is connected through ether linkages to the phthalimide moities. It is now necessary to convert the imides to anhydride structures. This is done by reacting the bis-phthalimide with phthalic acid in an exchange reaction that also generates the N-methylphthalimide for nitration to the starting material. In the nitration, isomers are formed and a separation is necessary. In the next step the dibasic acid moieties are dehydrated to give anhydride groups, and it is this di-anhydride which is the starting material for the poly(ether imide). Reaction of it with meta-phenylenediamine in an interfacial polymerization provides the product. In this polymerization the amine is used as a hydrochloride in water whereas the di-anhydride is dissolved in methylene chloride. Octadecylamine is included as a chain stopper, for the molecular weight must not be too high or else this polymer too will be intractable. This is representative of the highly sophisticated chemistry that will characterise polymer developments in the future.

Another example relates to polymer combinations. There has been much work on combining polymers in an attempt to achieve the best properties of both. Compatibility is obviously a key property. Chemists at DuPont conceived the idea of combining two incompatible polymers, high density polyethylene and nylon. This combination as a melt leads only to two phases on cooling. The creativity is embodied in a chemical "nail" to hold the two polymers together. This "nail" does not make the polymers compatible. It simply holds one to the other to keep them from separating. The "nail" is a graft copolymer in which acrylic acid is grafted to high density polyethylene. The polyethylene portion of the copolymer associates by physical bonding with the polyethylene component. The acrylic acid function, which is highly polar, associates with the polar polyamide and may even react with the terminal amine groups. Thus the copolymer holds the two incompatible materials together. When the melt cools, the polyamide, which is the minor component, plates out in overlapping layers within the polyethylene matrix to form a barrier. DuPont calls their new product "Selar" and describes it as a new barrier resin for the manufacturer of plastic bottles.

The point of these examples is that within maturity in an industry there may be creativity. The creativity described here is less than a decade old. It is my contention that this kind of creativity can be expected to continue in the future and may provide a buffer against the debilitating effects of the maturity of the industry.

SUMMARY

Two factors will affect the organic chemical industry in the future. One is the potential petroleum and natural gas shortage on which ninety percent of the industry is based. The other is the maturity of the industry. Both of these factors have motivated creativity of a type not even contemplated as little as even a decade ago, and this paper contains examples of it. This creativity can be expected to continue in the years to come and will mold the shape of the organic chemical industry of the future.