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NEW TRENDS IN CATALYSIS<sup>1/</sup>

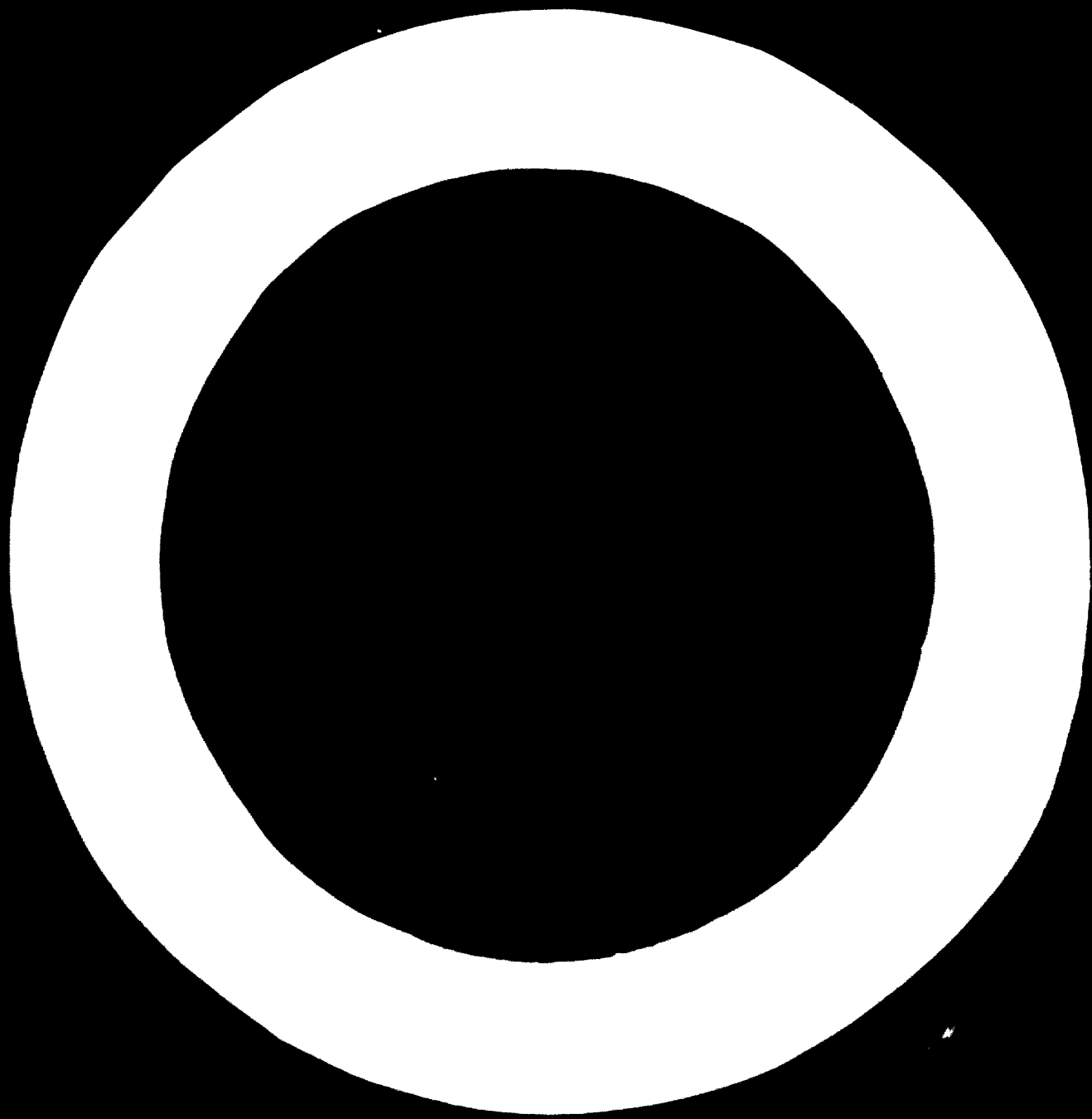
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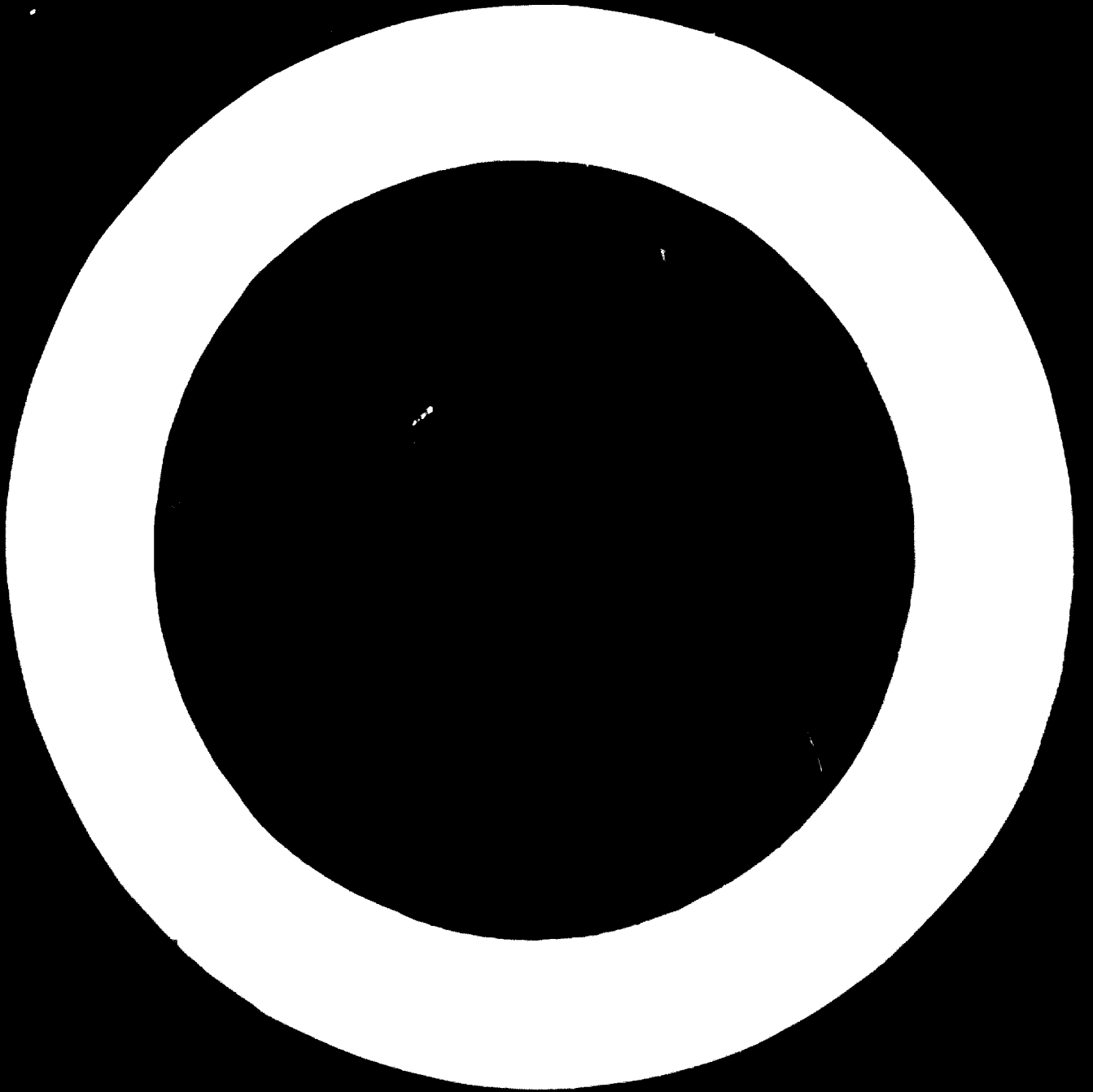
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## I. INTRODUCTION

Although it is advisable for developing countries to buy proven know-how, there is always the danger of buying processes that are obsolete. Many obsolete processes may actually be in use the world over, but their capital investment has been written off long ago and therefore they can compete with more modern processes.

If, on the other hand, the investment has to be done from the beginning, it is important to buy the most modern process which, however, must have proven itself technologically. Also local conditions, like the price of power, the size of the plant and the presence of certain raw materials, are of great importance in defining the choice of process to be used. Therefore, we want to give in this paper some examples of chemical processes which, by the improvement of catalysts, have undergone or will undergo drastic changes.

A great research effort has been invested the world over in homogeneous catalysis and, in spite of original pessimism in some quarters, processes have started to appear which compare favorably with the parallel processes, using heterogeneous catalysts.

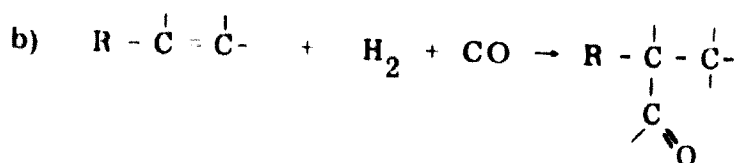
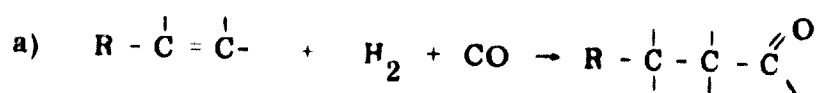
Improvements in existing heterogeneous catalysts have also brought down drastically the reaction temperature and pressure of some processes, but this does not always necessarily mean that the new process is better under all conditions.

We shall give some significant examples of processes where new catalysts have been developed, and instead of giving an exhaustive review, intend more to give some typical examples as to which factors, from the chemical point of view, have to be taken into account when one considers buying new technology.

## II. EXAMPLES

### 1. The OXO-Process (Hydroformylation)

The OXO-synthesis is concerned with the addition of CO and H<sub>2</sub> to a double bond and two isomeric products are usually formed:



Because, for many applications, the linear product is the more desirable one, the task of the catalyst is to give a maximal linear to branched ratio. Moreover, it is often the alcohol and not the aldehyde which is the desired product, and a catalyst which not only catalyzes the hydroformylation but also the hydrogenation of the aldehyde into alcohol, is even more preferable.

The classical catalyst for this reaction is based on cobalt, which is brought into the reaction mixture in the form of one of its salts. The active catalyst has been shown to be cobalt-hydrogencarbonyl HCo(CO)<sub>4</sub>, which is soluble in the reaction mixture. So we are concerned with a homogeneous catalyst, and one of the important features of the process therefore is the recovery of cobalt.

One of the pioneers in improving this process has been the Shell Company, which improves the performance of the cobalt catalyst by adding extra ligands which are almost exclusively tertiary organophosphines, R<sub>3</sub>P. Although hundreds of ligands are claimed to be effective in the patent literature, it seems that tributylphosphine and tricyclohexylphosphine are the ones actually used. Although the reaction has to be run at more severe conditions, using these catalysts, they give a higher normal to branched ratio and also hydrogenate part of the aldehydes formed.

A newer development is the use of rhodium instead of cobalt. Rhodium is one of the most expensive metals known, and a process using this metal as a catalyst is



only possible when catalyst losses are brought down to the absolute minimum.

It has been shown that monovalent rhodium in the presence of triphenylphosphine is very efficient in catalyzing the hydroformylation reaction. It is possible to use concentrations in the range of  $10^{-3}$  -  $10^{-4}$  M, to work at relatively low pressures, and to obtain high linear to branched ratios. Especially when done with an excess of triphenylphosphine, the linear product is almost formed exclusively. Only aldehydes are formed and no alcohols, and higher boiling condensation products are less prominent with the rhodium catalyst than with the cobalt catalyst.

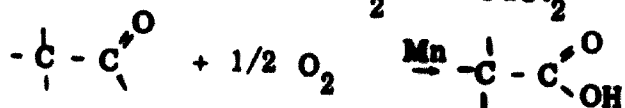
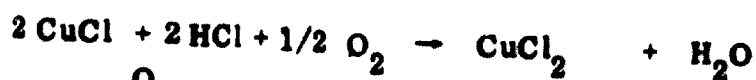
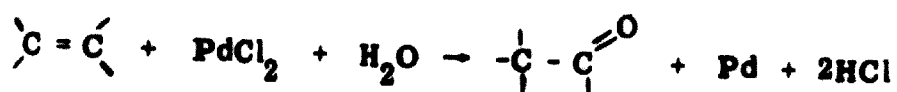
If low boiling products are formed only, no catalyst separation is necessary and the products can be distilled straight out from the reaction mixture. The catalyst does not decompose under these conditions.

These features are so advantageous that it is rather probable that OXO-technology will appear on the market in the near future, using rhodium catalysts instead of cobalt ones.

## 2. The production of Acetic Acid

The classical way of producing acetic acid is by the oxidation of paraffins, especially n-butane. Cobalt- and manganese salts are the catalysts used, and the reaction is run in the liquid phase, using a solvent. The oxidation is not very specific and many by-products have to be removed.

A serious competitor for this method is the Wacker process, which can be indicated as follows:

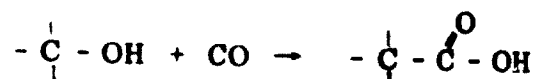


Palladium chloride oxidizes ethylene to acetaldehyde and is reduced itself to palladium metal. Palladium metal is oxidized by copper chloride. The cuprous chloride formed is oxidized by air. This means that in the net reaction, ethylene is oxidized by air to acetaldehyde. Acetaldehyde can be oxidized into acetic acid, using a manganese acetate catalyst.

The same Wacker process is used for producing vinyl acetate, when a mixture of ethylene, acetic acid and oxygen is led over a palladium catalyst. It is even possible to produce the acetic acid in situ and to produce vinyl acetate from ethylene, air and water directly.

There exists a liquid phase process, using a homogeneous catalyst and a gasphase process, where the palladium catalyst is precipitated on a carbon or alumina support. It seems that the heterogeneous gasphase process has better economical chances, because of the inevitable catalyst losses of the homogeneous process which are to be prevented when using an expensive material like palladium.

The newcomer in this field is the Monsanto process of making acetic acid out of methanol and carbon monoxide:



According to the patent literature, the catalyst is based on rhodium. This process is said to have important economic advantages over the Wacker process.

### 3. The production of Ammonia and Methanol

The changes in ammonia production in recent years are mostly of a technological nature. Because of improvements in the manufacture of synthesis gas, which enables operation of the plant at 35 atmospheres instead of 5 and the use of centrifugal compressors which can compress the gas in one step to 200 atm., the ammonia synthesis nowadays is run at 200 atm. instead of 300 atm. earlier. The lower conversions per pass are more than compensated by the greater ease of recycling the

gases. The classical synthetic ammonia catalyst has not undergone drastic changes.

The classical way of synthesizing methanol from synthesis gas uses technology similar to that used in ammonia synthesis. Temperatures of several hundred degrees Celsius and pressures of several hundreds of atmospheres are used. In this case, new catalyst development has caused a decrease in working temperature and pressure. By using zinc-copperchromites instead of the classical zinc-chromite catalyst, it became possible to design plants that work at 50 atm. pressure and about 250°C.

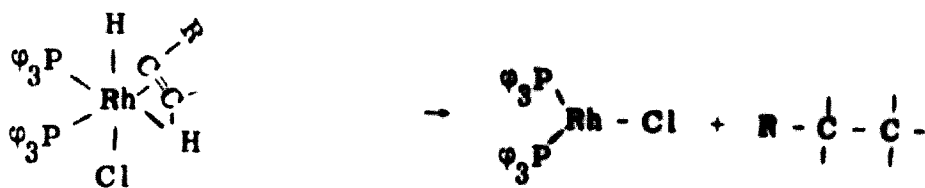
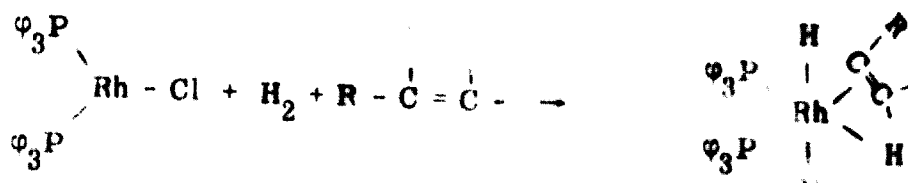
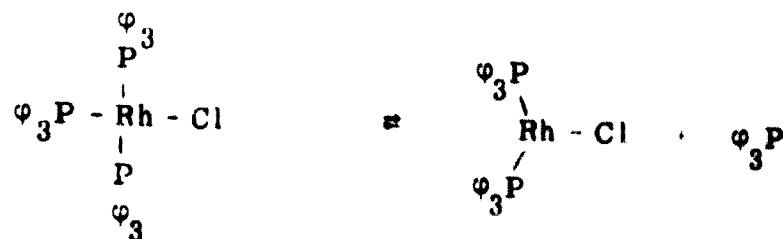
These technological and chemical considerations have some interesting implications. As in a developing country, the need for ammonia is probably felt in an earlier stage than the need for methanol, because ammonia is a fertilizer ingredient and methanol a chemical intermediate, one might consider planning the ammonia plant such, that at a later stage it can be converted into a methanol plant, when ammonia capacity has to be extended. In such a case it would not be advisable to use the low pressure methanol technology. But also in other cases the fact that a process can be run at lower pressures and temperatures does not always mean an economical advantage, and this has always to be weighed carefully against factors like the price of electrical power and the turnover of the plant.

#### 4. Hydrogenation

Hydrogenation is an operation which is used in many processes and ranges from the massive hydrogenation of benzene into cyclohexane to the specific partial hydrogenation of fatty acids, which is necessary in modern margarine manufacture.

Although heterogeneous catalysts based on the classical noble metals and nickel and cobalt still dominate the field, the new developments in homogeneous hydrogenation are so rapid that we would like to discuss some aspects of them. It is quite conceivable that some homogeneous catalysts might find a place in this field in the near future.

The best studied of all homogeneous hydrogenation catalysts is trisphenylphosphinerhodiumchloride, which is supposed to work as follows:



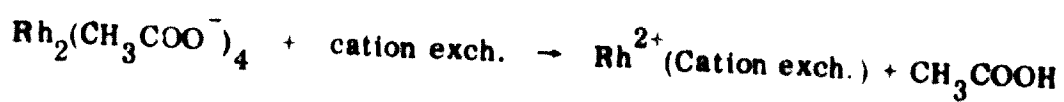
The tris(triphenylphosphine)rhodiumchloride loses one triphenylphosphine ligand in solution, and the resulting bis(triphenylphosphine)rhodiumchloride complexes with one molecule of hydrogen and the olefin. The hydrogen adds to the double bond of the olefin in the complex shell and the paraffin thus produced leaves to make place for a new set of hydrogen and olefin.

This catalyst works efficiently at ambient conditions of pressure and temperature in organic solutions at very low concentrations.

The fact that the catalyst is a homogeneous one might be a drawback in many cases, because the expensive catalyst has to be recovered quantitatively.

Several patents describe methods to bind the homogeneous catalyst to an insoluble carrier, by which means this disadvantage can be circumvented.

For instance, the carboxylates of noble metals like rhodium, ruthenium, iridium or rhenium in their bivalent states are good hydrogenation catalysts in the presence of triphenylphosphine in methanol solution. If the carboxylate anion is replaced by a cation exchanger:



we get a heterogeneous catalyst, which, in the presence of triphenylphosphine in methanol solution is capable of hydrogenating olefins. In such a case we get catalysts that combine the virtues of a homogeneous and a heterogeneous catalyst in such a way that, after the reaction, the catalyst can be removed by filtration.

Other very active hydrogenation catalysts can be obtained by the combination of a transition metal salt and a derivative of lithium aluminium hydride. Especially salts of titanium and cobalt are extremely effective.

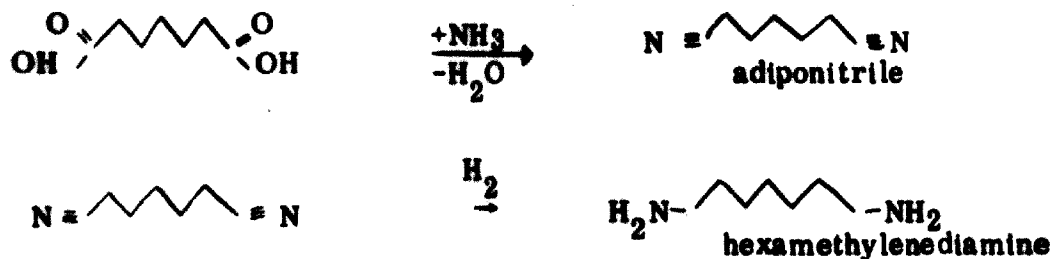
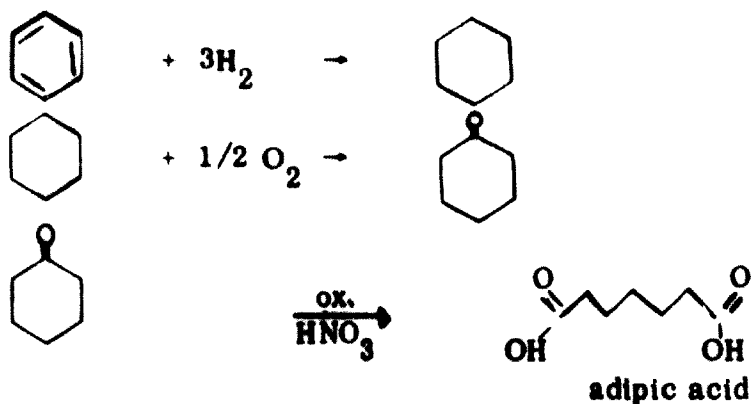
For instance, a mixture of cobalt bromide and  $\text{LiAlH}(\text{OtBu})_3$  in a ratio of one to four at a concentration of 3 m mol/L is capable to hydrogenate cyclopentene in tetrahydrofuran at a rate of 0.44 mole  $\text{H}_2$ /Liter/min., which is extremely fast.

There are numerous examples of other very active homogeneous hydrogenation catalysts and certainly several of them will find their way into technological hydrogenation processes in the near future.

##### 5. Nylon Intermediates

The classical way of producing nylon intermediates is based on cyclohexanone, which is obtained by the oxidation of cyclohexane which, in its turn, is based on benzene.

In short:



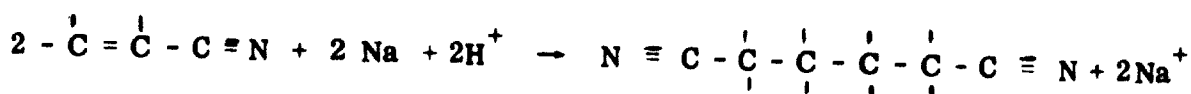
The production of adipic acid following this route is quite satisfactory, and the improvement which is sought is to perform the oxidation of cyclohexanone by air and not by nitric acid, which might lower its price somewhat.

Hexamethylenediamine, on the other hand, is too expensive this way, and several other routes are being tried, some of which will appear as available technology in the near future.

One of the ways of obtaining this is by the dimerization of acrylonitrile, itself a raw material for artificial fibres. Many catalysts have been developed to execute this dimerization, but none seems to be too successful. An electrochemical route has been developed by Monsanto and is in actual production:



Another interesting possibility has reached the pilot stage, and is to utilize the sodium amalgam, which is formed during conventional salt electrolysis for chlorine production:



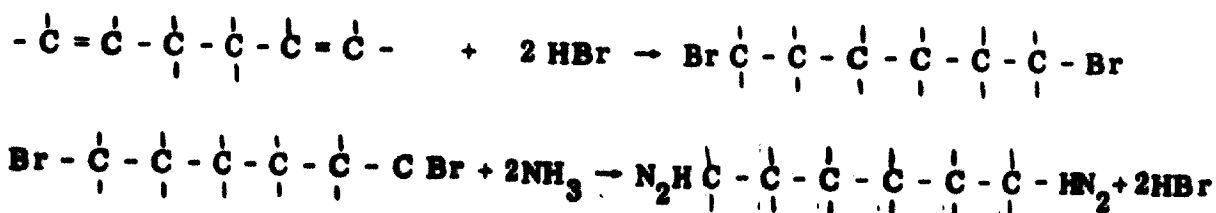
Because in most cases the sodium amalgam is anyway decomposed with water to give caustic soda solution, there is a possibility here of utilizing the sodium amalgam for adiponitrile production and still ending up with a caustic soda solution.

One drawback with all methods that have adiponitrile as an intermediate is the rather cumbersome reduction of nitrile to primary amine, which suffers from short catalyst lives and the formation of secondary and tertiary amines.

There are patents that describe other methods of synthesis where the amine is formed not via a nitrile. Propylene can be dimerized rather efficiently using a bismuth catalyst:



This diolefin can be converted into hexamethylenediamine by the addition of HBr and reaction with ammonia:

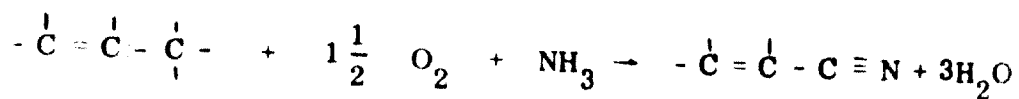


Although the technology for converting a terminal double bond into a primary amine with the help of HBr is known and has been used for years to produce Nylon Eleven, no processes are on the market at the moment to produce hexamethylene

diamine this way, but they might well be developed in the future.

### 6. Amoxidation

The production of acrylonitrile by the oxidation of propylene in the presence of ammonia in a fluidized bed reactor, has become big business in the last decade:



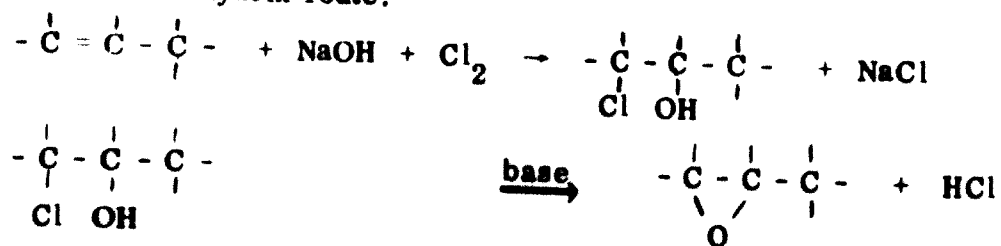
The catalyst most used is bismuth molybdate, which gives about 10% of acetonitrile as a by-product. The Sohio Company in the United States has developed a uranyl antimonate catalyst, which gives more acrylonitrile and less acetonitrile. The Montecatini Edison Company in Italy has developed a Tellurium Molybdate catalyst which seems to be as satisfactory as the other catalysts in use.

A drawback of the amoxidation process is that its minimum size of economic production is rather large, as is the case with most fluidized bed processes.

Therefore, a process to make hexamethylenediamine from acrylonitrile is so important because the same acrylonitrile plant delivers raw materials for acrylic fibres as well as nylon.

### 7. Epoxidation

The epoxidation of ethylene with air to give ethylene oxide is an established process, using silver catalysts. The direct oxidation of propylene, however, according to this method, is very difficult and most propyleneoxide is still made according to the established chlorohydrin route:

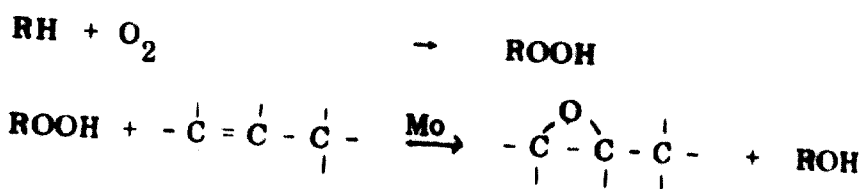




Several new processes have recently been developed or are being developed. One is to do the same chlorohydrin reaction in an electrochemical cell. This route might be important for countries which have not enough chlorine available.

By electrolysis of NaCl, chlorine is formed at the anode, is brought into contact with propylene and forms chlorohydrin. This diffuses to the cathode, where, because of the high pH, it is decomposed into propylene oxide and NaCl is formed again. The net process is thus an electrochemical oxidation of propylene into propylene oxide. This process is under development and might, under special circumstances, be competitive with the chlorine route.

An entirely different process has been developed by Scientific Design Inc. It is based on an interesting catalytic reaction between organic hydroperoxides and an olefin:



A hydrocarbon is oxidized to a hydroperoxide with air and the hydroperoxide reacts with propylene to give propylene oxide and an alcohol. Compounds of molybdenum seem to be the best catalysts for this latter reaction.

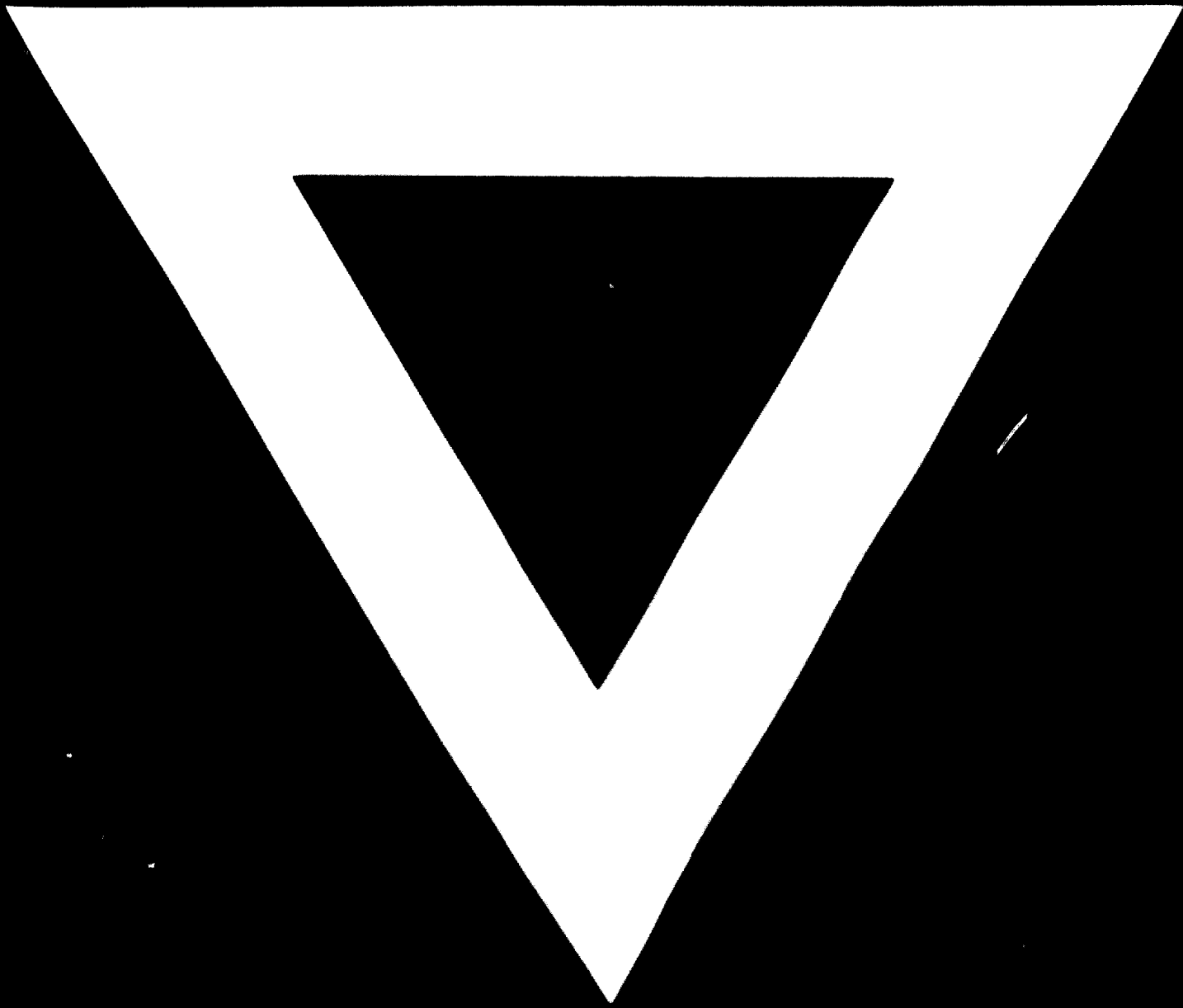
One of the disadvantages of this process is that the production of propylene oxide is coupled with that of an alcohol, for which a market has to be found. If, for instance, ethylbenzene is the hydrocarbon, styrene can be produced by dehydration of the alcohol. Under certain conditions it might be attractive to produce styrene and propyleneoxide in one and the same plant.

Several companies are still active to reach the point where propylene can be oxidized directly with air, the same way as is done with ethylene, and technology based on this direct oxidation might well be available in the near future.

### III. CONCLUSIONS

In this paper we have described some of the newer trends in catalysis for the production of chemicals. Any choice concerning the type of process to be bought is dependent on local conditions. An electrochemical route, for instance, might be advantageous in countries where electrical power is cheap and only a small factory size is necessary for the time being. OXO technology and the production of ammonia and methanol are in a state of flux, and more modern technology might be available from year to year. Nylon production can be coupled with salt electrolysis and acrylonitrile production, and styrene with that of propylene oxide. Although processes which give coupled products are not always attractive to the big producer in a developed country, they might be attractive to a developing country. Therefore, local conditions dictate the choice of processes to be bought and the kind of trends as described here are important to know for those who have to make this choice in the near or more distant future.





**16. 7. 74**