KEITH SMITH

HOW GREEN IS MY VALIUM?

(Are Chemicals Kindly or Killers?)

University College of Swansea

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INAUGURAL LECTURE

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by

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HOW GREEN IS MY VALIUM?

[Are Chemicals Kindly or Killers?]

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Introduction

The world of chemistry may appear to many to be a mysterious, unintelligible, perhaps even sinister world. Yet chemistry impinges in a major way on the lives of everyone, and it is important for chemists to explain what they do to the wider audience. An Inaugural Lecture provides an opportunity to do just that. The challenge, however, is to find a topic which is chemically meaningful and yet still capable of attracting wider attention. With the growth of public interest in the protection of the environment, it is hoped that the choice of a "green" topic may serve that purpose. Apologies are due to the author, Richard Llewellyn, for corruption of the title of his famous novel "How Green was my Valley".

In order to develop the theme of the lecture, it will be necessary to begin with an explanation of what is meant by the term "chemicals", in particular "organic chemicals", and to explain what organic chemists do. Several myths will then be dispelled in order to allow a sensible treatment of the impact of chemistry on the environment. Finally, some of the research interests of the author will be discussed.

What are (organic) chemicals?

Chemistry is the study of matter - all kinds of matter! Chemicals are the individual components which make up such matter. Thus, the land, the sea, the air, and the living organisms which inhabit them, are all made up entirely of chemicals.

For millenia man has taken advantage of the particular properties of the chemicals in his environment to help improve the quality of his life - for example, using the combustible materials in wood as a source of energy for cooking and providing warmth. However, the really dramatic impact of chemistry has taken place over the last hundred years or so, during which chemists have made millions of new chemicals which were never available before. This has led to the widespread but mistaken belief that "chemicals" are specifically man-made materials. Furthermore, the preoccupation of the press with disaster stories has led to the equally unfortunate view that "chemicals" are inevitably harmful.

The real situation is more accurately reported in the book *"C for Chemicals"* published by Green Print, the opening paragraph of which is given in Figure 1.

> "It is impossible to avoid chemicals in everyday life. Indeed we ourselves are made up of thousands of complex chemicals, which interact in subtle ways to keep our bodies working. *When we use the term 'chemicals', however, we often mean artificial substances* used in industry and the home to maintain the standard of living and lifestyle of the (usually) developed world. *The term often has a derogatory tone to it, despite the fact that the majority of known substances have minimal or zero adverse effects* on health and the environment".

Figure 1. The opening paragraph of *'C for Chemicals'* by M. Birkin and B. Prince, Green Print, 1989, p.1.

All chemicals are composed of one or more building blocks called atoms. There are in total about 100 different types of atoms (see Figure 2), of which about half are rarely or never encountered by the general public. The enormous variety of available chemicals is possible only because of the huge number of possible permutations in which several different types of atoms can be combined in different ways to form larger groupings called molecules. These molecules are the fundamental particles corresponding with the term "chemicals".

The term "organic chemicals" refers to molecules which contain carbon atoms (symbol C) and one or more different types of atoms, typically hydrogen (H), oxygen (O), nitrogen (N) and chlorine (Cl). As the name implies, the molecules associated with living things are primarily organic chemicals and it was for this reason the term was coined. Indeed, it was originally believed that organic chemicals possessed some "vital force" derived from nature, which could not be attained artificially; thus, "organic" chemicals could be obtained only by extraction from

living or once-living things or by chemical conversion of such extracted materials, thereby transmitting the "vital force" to the new chemicals. This notion was firmly laid to rest by the chemists Wöhler and Kolbe in the 1830's and 1840's. Curiously, many people nowadays hold a similar belief, perhaps again rooted in theology, that it is theoretically impossible to generate new life forms entirely by artificial means, but the technical expertise needed to synthesize all of the essential chemical components of living organisms is already available. It is surely only a matter of time before understanding of cell structure and organization advances to the point where the *ab initio* synthesis of a completely novel living cell, and thereby of a new life form, becomes a reality. That discussion, however, is beyond the scope of this lecture.

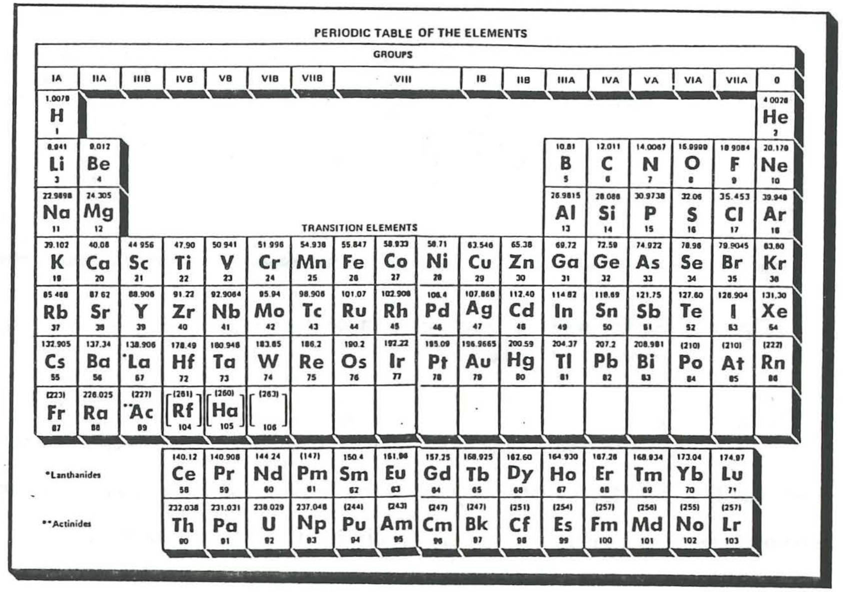


Figure 2. The different types of atoms are all given different symbols.

Although organic chemistry deals only with the chemistry of carbon-containing substances, *there are many more chemicals which contain carbon than do not.* The number of known organic chemicals already runs into several millions and is increasing rapidly all the time.

Therefore, it is necessary to have some means of depicting the structures of the different molecules if the chemistry is to be discussed. Figure 3 shows several ways of doing this.

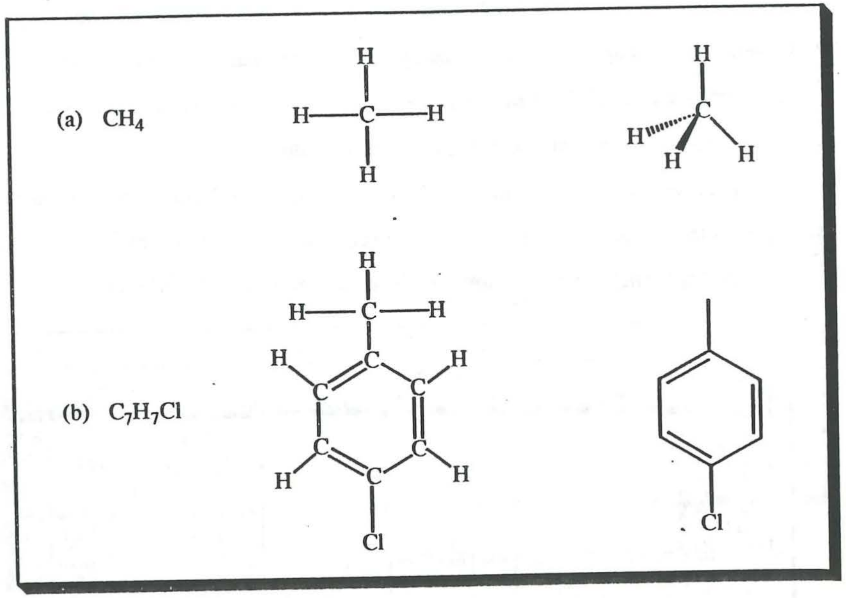


Figure 3. Several ways of depicting the structures of organic chemicals: (a) methane; (b) *para*-chlorotoluene.

Organic chemists have devised many ways for changing one chemical into another, and have thus been able to generate many new organic chemicals never found in nature. The procedures involved are not so strange, and are discussed in the following section.

What do organic chemists do?

The processes carried out by organic chemists are quite similar in many ways to the familiar processes of the kitchen. For example, organic chemists often want to separate organic chemicals one from another, a process known as purification. In order to do so they make use of the different properties of the chemicals, such as their solubilities in a particular solvent, their boiling temperatures, or their ease of adsorption by solid adsorbents. They apply techniques

such as extraction, filtration, distillation and chromatography to effect the separation. The combination of solvent extraction and filtration is commonly used in the kitchen to produce a clear brown solution of tea from tea leaves or coffee from coffee grounds. Although the extracts obtained in the latter cases are still not pure, they are less complex mixtures than the original tea leaves or coffee grounds because many unwanted components have been left behind in the tea strainer or coffee filter.

Organic chemists often want to mix chemicals together to produce a mixture having particular, desirable properties. There is a close analogy with adding milk and sugar, in exactly the right amounts, to produce the perfect cup of tea. Another reason for mixing chemicals is in order to carry out chemical reactions. The chemicals must be carefully metered, for example by weighing, so that the correct proportions for the desired reaction are present. In the same way, the cook is careful to mix the correct ingredients in the proper proportions.

In order to encourage reactions to occur, the organic chemist may need to supply energy to the mixture, by heating or irradiation with light, for example. The cook does exactly the same with heat or microwave energy.

Finally, the organic chemist needs to know what he or she has accomplished. Whereas the cook has to be satisfied simply by the appearance or taste of the finished product, the chemist uses a battery of sensitive analytical techniques to determine the structures and measure the quantities of all of the chemical components produced. It is the *understanding* gained by such detailed analysis of the results of experiments that differentiates the chemist from the cook. Nevertheless, cooks undoubtedly carry out organic chemistry.

In reality, therefore, chemistry is neither mysterious nor sinister, but involves processes which are quite familiar. There are several other myths which also need to be dispelled, as discussed in the following section.

Dispelling the myths!

It is imperative to correct some common misconceptions if the role of chemistry is to be sensibly discussed. For example, it is widely implied that *chemists are intent on destroying the* *planet.* Figure 4 shows a typically damaging commentary, the more significant for its appearance in a book intended for children.

> "Out go the traditional farming methods like 'crop rotation' which have been used successfully for centuries. *In come the chemists with artificial fertilizers and killer sprays,* all at enormous cost to wildlife, the environment and, possibly, our health."
>
> The Blue Peter Green Book, p.10.

Figure 4. Extract from 'The Blue Peter Green Book', BBC Books, 1990, p.10.

It is not immediately obvious from a statement like that in Figure 4 that the role of chemists has been to develop the means of improving both the yield and quality of crops in order to provide sufficient food for a rapidly expanding world population now standing at over five thousand million. Their self-evident success in this endeavour is ignored and instead they are blamed for the fact that large scale use and occasional abuse of fertilizers and pesticides leads to other problems. Yet it is chemists that are needed for the development of the next generation of agrochemicals, such as pheromones, which will be more selective, less toxic and even more necessary than the present ones. The adverse impression of chemists given by the media does not help to encourage young people to study chemistry and enter the profession so that future problems can be tackled.

Another common misconception is that *natural materials are wholesome whereas 'chemicals' are unhealthy*. Firstly, the statement itself is somewhat nonsensical in that natural materials are also chemicals, but even if the term 'non-natural chemicals' were to replace 'chemicals' the statement would be equally difficult to justify. If natural materials are so wholesome, why do people avoid eating death cap mushrooms, deadly nightshade berries or the leaves of the foxglove? Clearly, it is because they are well known to be highly poisonous, despite being natural. Equally, many non-natural chemicals appear to be perfectly safe (see Figure 1).

It might, however, be argued that the above examples are unrepresentative, that acutely toxic plants have been excluded from diet for centuries and do not invalidate the major conclusion that those natural foods which are eaten are healthy. Equally, the fact that many 'synthetics' have no known adverse effects does not change the fact that introduction of additional ones may introduce new adverse effects. Underlying such beliefs is the notion that man has somehow evolved to cope with the chemicals in natural foods but has not had time to do so for synthetic ones.

Unfortunately, even this argument cannot be sustained. With the need for higher yields to cater for a growing population and the desire for a greater variety of foods many new, genetically different crops have been introduced. These produce a somewhat different cocktail of chemicals than long established crops. Also, foods and spices are now transported all around the world, to be used by peoples whose ancestors never experienced them. It is hard to imagine that such peoples can have evolved to cope with the chemicals in these new foods so quickly. In any case, there are many examples of long established foods giving health problems - most notably milk (the majority of adults in the world show some intolerance to milk) and wheat.

Of course, some people do show intolerance to some synthetic chemicals and it would be sensible to ban any food additives which cause adverse reactions in a significant number of people, especially if the use were merely for cosmetic purposes, as in the case of colourings. It is also proper for people deliberately to avoid foods which have additivies which they do not like. However, to argue the general case that synthetic chemicals are harmful and natural ones wholesome is both facile and false and could, indeed, result in unacceptable risks if the argument were translated into practice. The words of Leslie Kenton, in her foreward to Maurice Hanssen's *'E for Additives'*, are more balanced (see Figure 5).

A third common misconception is that *chemistry causes pollution*. Since all materials are composed of chemicals, it is a truism to say that chemicals cause pollution, but this fails to attempt any analysis of the problem. The fact is that people cause pollution. Even primitive peoples living entirely off the land produce waste. If they are few in number the earth can cope with the small amount of waste easily enough, but as the population grows to a point where millions of individuals live in an area of a few square miles, as with modern cities, the direct biological waste which they produce becomes an enormous problem. The immediate locality can no longer cope with it by natural decomposition processes within the necessary timescale. Chemical processing becomes inevitable. Furthermore, food, clothing and building materials have to be produced to cater for the population. Reliance on natural materials (e.g. wool and furs for clothing, native crops and animals for food, and wood for building) would cause immense environmental damage to a vast area.

> "I would prefer to live in a world where we harvested our foods fresh from the earth, ate them immediately and never had to give a thought to food preservatives, artificial emulsifiers and stabilizers, anti-oxidants and permitted colours. Alas, we do not live in such a world. High technology food production and elaborate chains of food distribution have created a situation in which *food additives are necessary*."
>
> L. Kenton.

Figure 5. Extract from the foreward to 'E for Additives', Thorsons Publishers, Wellingborough, 1984.

The problem is further exacerbated when the population wants a standard of living which is higher than subsistence level. The only way to cater for such needs is to develop factory methods of production which can produce large quantities of goods on a relatively compact scale. It has been estimated that to match the output of one of I.C.I.'s man-made fibre producing factories with wool would require sheep grazing over an area the size of Belgium. The factory might produce effluent, but the scale of environmental impact is much less than that which would result without the factory methods.

Nevertheless, factories do pollute, even if the scale is less than would be the case in their absence. Does this not demonstrate that chemistry causes pollution? No! In an absolute sense all human activity creates pollution; the significant point is the direction of change. It is important to develop in a way which reduces rather than increases the levels of pollution. Countries which are chemically more advanced are demonstrably less polluted than those which are less so, showing that advances in chemistry cause a relative improvement in pollution levels.

The sordid scenes of East European industries which have appeared since the breakdown of the Iron Curtain, for example, should be compared with the situation in countries with the most highly developed chemical industries, such as Switzerland. It is also readily evident that pollution levels in Britain are lower today than they were thirty to fifty years ago. No longer do thick smogs afflict our cities as they used to, and heavy industrial pollution of the type which scarred the Lower Swansea Valley until the second world war is a thing of the past.

There is no cause for complacency about pollution, but it is clear that *advances in chemistry have actually served to reduce pollution* at a time when total production of chemicals has substantially increased. Therefore, it is necessary to take a more considered look at the effect of chemistry on the environment than the usual tabloid level of analysis.

Chemistry and the Environment.

As explained above, advances in chemistry bring some relief from the high levels of pollution which would otherwise occur as the population expands. They do so in three major ways. Firstly, *chemistry creates wealth*, which permits expenditure on better technology such as effluent treatment and fail-safe design. In Britain, this creation of wealth is also fundamental to the economy - in the first half of 1990 the balance of trade in chemicals (excluding oil) was in *surplus* by £1,200M (even more if oil is included), whereas the overall balance of trade for the country was in *deficit* by several thousand million pounds.

Secondly, *chemistry helps control population growth*, both directly through production of contraceptive pills and devices, and indirectly by reducing the pressures which lead people to desire large families. These latter pressures arise as a result of dependency on offspring in later life, but increased longevity, better health and financial security in old age all contribute to reduce such dependency, and chemistry is largely responsible for all three factors. As yet these benefits have not fully extended to the developing world, where the population is still growing rapidly. It is this growth of population which presents the greatest threat to the environment.

Thirdly, there is a direct effect because *chemistry can provide new products which are environmentally friendlier and new processes which are intrinsically cleaner*. Whether such processes and products will be adopted may depend on fashion, economics or legislation, but chemistry can at least provide the means.

For example, pest control is vital for the success of any intensive farming operation, especially in the developing world, where food production is barely sufficient for the needs of the population and where insect infestation can lay waste to vast areas of crops in short periods. The first generation of chemicals for control of such pests were insecticides, i.e. they depended on toxicity for their effect. Compounds like DDT (Figure 6) were highly successful at controlling pests, but were rather persistent in the environment and therefore caused harm to other wildlife and even, potentially, to humans. The second generation of insecticides has been designed to reduce these risks. The pyrethroids, for example, which are synthetic variants of chrysanthemic acid (Figure 6), are not particularly toxic to mammals and after utilization break down into harmless constituents within days. Though they cannot be said to be completely harmless to the environment, because they can still destroy beneficial insects, they are far less damaging than first generation insecticides. Some idea of the magnitude of the danger from pesticides can be gained from the statements shown in Figure 7.

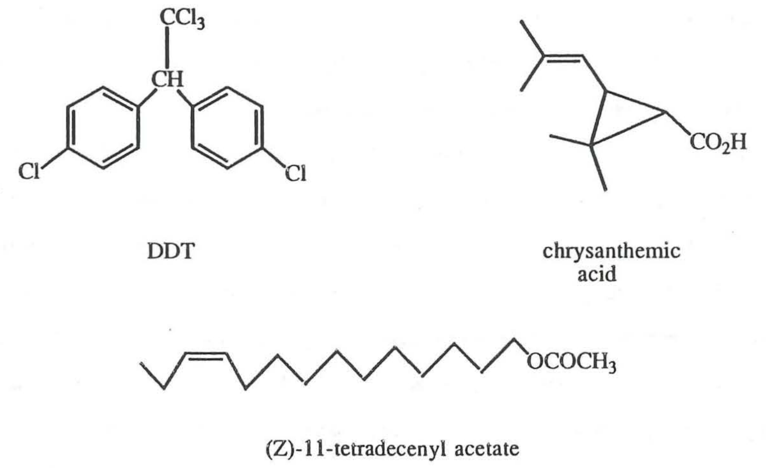


Figure 6. Three generations of pest-control chemicals

Even so, improvements in pest control are still sought and chemists are now well advanced with the third generation of chemicals for insect control, which include pheromones such as (Z)-11-tetradecenyl acetate, the sex attractant to the red-banded leaf roller (Figure 6). Pheromones have the potential to confuse insects to prevent them mating or to attract them to traps where they can then be killed with much smaller quantities of insecticides. They are not themselves toxic, are species-specific and can be used in much smaller quantities than traditional control agents. Pheromones have been isolated, identifed and synthesized by chemists.

> "Is there any real evidence, though, for widespread harm resulting from the use of garden pesticides? It has to be admitted that there is not a great deal."
>
> *'C for Chemicals,'* Green Print, 1989, p.49
>
> "In the agrochemical sector, quite amazing improvements have been made in reducing the negative impact on the environment. Over a fifteen year period, the quantity of active substances used on crops have been divided by a factor of 100, remaining just as effective".
>
> J.-M. Bruel, President of Rhône-Poulenc, *Chemistry and Industry*, 1990 (22) p.735.

Figure 7. Some comments about the use of pesticides.

When established chemicals are still required, superior methods of production can lead to reductions in environmental impact. For example, I.C.I.'s 'LCA' process for ammonia achieves major reductions in the emission of nitrogen oxides, NOx. It has been estimated that if all the world's ammonia production were to be converted to the LCA process, it would be the equivalent in NOx reduction of taking five million cars off the road (Chemistry and Industry, 1990, p.735).

Clearly there is still much room for improvement in the environmental impact of chemicals. Global problems like ozone layer depletion and warming caused by carbon dioxide build-up have only recently been seriously considered and they necessitate major changes in social attitudes if the trends are to be reversed. Furthermore, many factories, vehicles and homes pump out more waste products than is necessary, and some commercial products are more likely to damage the environment than is acceptable. However, it is chemists who have the major role to play in overcoming these problems and creating a cleaner, 'greener' environment. Even the researches of academic groups can have some influence, as discussed in the following section.

The Research Work of the Author.

The research interests of the author centre on the development of new or superior organic chemical reactions. The driving force is the desire to increase the knowledge base rather than to solve any particular commercial or environmental problems, and much of the work uses relatively esoteric chemicals like organolithium or organoboron species, which are rarely used on a commercial scale at present. Even so, it is still sometimes possible to see potential applications for the work.

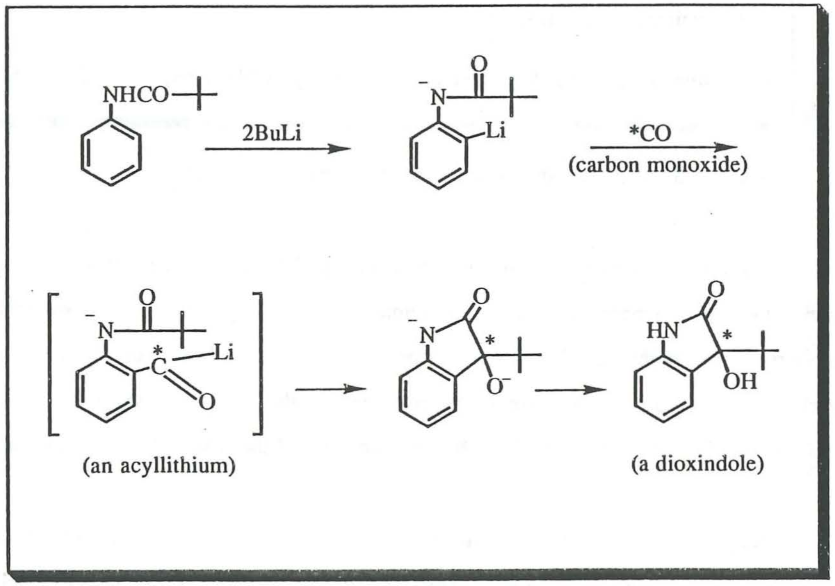
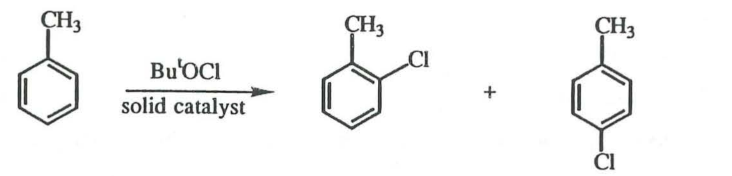


Figure 8. Internal trapping of an aromatic acyllithium.

For example, in the recently reported (*Angewandte Chemie*, 1990, **102**, 298) reaction of certain types of aryllithium species with carbon monoxide (Figure 8), which has provided the first demonstration of the synthetically useful generation and trapping of aromatic acyllithium species, there is potential in the field of medical diagnosis by a technique know as positron emission tomography (PET). In this technique a patient is fed a chemical which is known to locate in a particular organ such as the heart or brain (e.g. a drug used in the treatment of heart disease or brain disorders). However, instead of the ordinary form of the chemical being used, a form in which one of the atoms has been replaced by a radioactive form of the atom is used. While the chemical is located in the organ it emits radioactivity and this can be photographed with an x-ray camera, thereby allowing examination of the organ without invasive surgery. In order to give the lowest dose of radiation to the patient it is best to use a radioisotope with a very short half-life, and carbon-11 (half-life 22 minutes) is the ideal one. Carbon monoxide is one of the few chemicals available directly from a cyclotron in C-11 form and any reactions which can easily incorporate it directly into complex molecules with potential for use in PET studies are therefore valuable.

An area which might have greater direct environmental impact concerns the use of solid catalysts and supports. Entry into this area arose by chance following the observation of chemical changes during purification of a product mixture by chromatography on silica (a refined form of sand). Experimentation showed that silica was capable of transforming *tertiary*-butyl hypochlorite, an otherwise unreactive molecule under the conditions used, into a reactive species capable of chlorinating toluene (Figure 9). From a commercial viewpoint this is not a very attractive reaction because the reagent (reactive agent) is more expensive than chlorine itself. However, there is some potential for reducing environmental damage because at the end of the reaction all the unwanted by-products adhere to the silica, leaving the pure chlorotoluenes in the solvent, from which they are easily separated. The by-products can then be removed from the silica and recycled, and there would be negligible effluent.



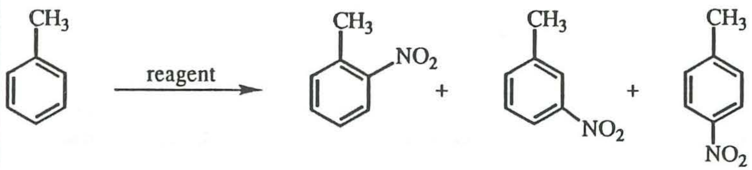
	2-chlorotoluene		4-chlorotoluene
silica	65	:	35
H Zeolite X	9	:	91

Figure 9. Chlorination of toluene over solid catalysts.

However, there are other solids which are more powerful catalysts than silica, for example acidic forms of zeolites. Furthermore, zeolites have highly crystalline structures which contain regular holes and channels. If reactions could be encouraged to take place within such pores then the geometrical restrictions imposed by the pores might allow some control over the reaction proportions. Indeed, use of acidic form zeolite X in place of silica resulted in the highest selectivity in favour of the 4-chlorotoluene isomer that has over been achieved (Figure 9) (*Synthesis*, 1985, 1157). Also, the reaction is extremely clean (100% yield of chlorotoluenes) and takes place at room temperature. According to a company which has costed the process it would result in substantial cost savings compared with current processes, but, of course, it would require substantial investment in new plant.

Even more significant from an environmental point of view would be to develop a better synthesis of 4-nitrotoluene (Figure 10). This product is manufactured in the U.K. to the extent of 30,000 tons per annum, but its synthesis also produces 60,000 tons of 2-nitrotoluene, which is of little value. At times, the latter chemical has been burnt to product the energy to drive the plant, but this would no longer be permissible. At the present time it is sold off cheaply for some purpose or other, but at other times it might have to be disposed of. Both economic and environmental concerns point to the need to find a reaction which increases the proportion of the 4-nitro component. The use of solid supports has again permitted such a reaction (Figure 10)

(*Tetrahedron Letters*, 1989, **30**, 5333). Unfortunately, the reagent used in this case is too expensive for commercial use unless or until cheaper ways of producing it can be found.

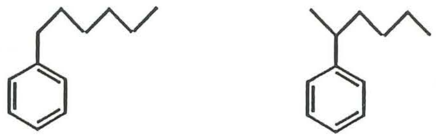


H_2SO_4/HNO_3	65	:	2	:	33
$PhCO_2NO_2$/HMord	31	:	2	:	67
	2-nitro-toluene		3-nitro-toluene		4-nitro-toluene

Figure 10. Nitration of toluene by different methods.

In one final example, alkylbenzenes are produced in bulk for conversion into detergents. There would be advantages if the benzene part of the molecule were attached to the end of the alkyl chain (see Figure 11), which would give products which had better viscosities and easier biodegradability. Unfortunately, direct alkylation of benzene produces molecules with the benzene ring attached at an internal position (Figure 11) rather than at the end. Some current work in Swansea is concerned with the development of a successful process for producing the terminally substituted compounds.

Thus, even work carried out in an academic environment and with mainly academic aims can result in discoveries which might lead eventually to new commercial processes which are environmentally friendlier than the traditional ones.



1-phenylhexane
(terminal attachment)

2-phenylhexane
(internal attachment)

Figure 11. Different types of alkylbenzenes.

Conclusions

Although by definition pollution involves chemicals it is far too facile to make chemistry and chemists the scapegoats for its cause. The real major causes of pollution are the rapid expansion of the world population and the desire of individual members of society to enjoy a higher standard of living, both of which lead to greater consumption and increased waste. However, pollution levels have actually been attenuated by the activities of chemists and chemists continue to search for new processes and products which will help to reduce them still further.

The responsible elements within the 'Green' movement are fully aware of the link between scientific advancement and the improved standard of life, including a cleaner environment, which so many people now enjoy. Their intention is not to damage science in general nor chemistry in particular, but to increase awareness of how individual behaviour can influence the environment, and to identify activities where there is room for greater attention to environmental impact. The chemical industry should listen to such approaches and generally put environmental impact even higher on its list of considerations when investing in plant or developing processes. It is clear, however, that such considerations are already to the fore, as evidenced by a series of articles by

leaders of the chemical industry in their house journal (*Chemistry and Industry*, November 19, 1990).

Unfortunately, there is also another wing to the 'Green' movement which implies that all scientific, and particularly chemical, advancement is bad. This group appears to want society to return to a pre-industrial situation with a subsistence lifestyle based on 'natural' materials. It never misses an opportunity to denounce the chemical industry, to criticize scientists or to point out the dangers of 'chemicals'. No-one can deny that chemicals can be dangerous, that accidents do occur, that errors of judgement are made or that scientists are capable of ordinary human failings. However, to extrapolate from that to suggest that all chemicals are harmful, that the chemical industry is corrupt and that chemists are all evil is a nonsense.

Unfortunately, such suggestions find a sympathetic hearing with the media, which rely upon scare stories, disasters and natural human fears to sell their wares. As a result, much of the reporting which relates to chemistry is facile and hurtful. Even more importantly, it is damaging to the environmental cause it claims to espouse because it deters young people from wanting to be involved with chemistry, and chemistry is the key to the solution of many of the world's environmental problems. It is time for chemists to begin to counter the black propaganda!