Review Commentary
Heterogeneous catalysis of organic reactions

Pierre Laszlo

Laboratoire de Chimie Fine aux Interfaces B6, Université de Liège au Sart-Tilman, B-4000 Liège, Belgium
Département de Chimie, École Polytechnique, F-91128 Palaiseau, France

ABSTRACT: A decade's worth of work is reviewed: building on the demonstrated prowess of heterogeneous catalysis in industrial organic chemistry, the author's laboratory devised efficient catalysts for a number of organic reactions, based on aluminosilicates such as clays and zeolites. This review also spells out, at a time when creative research is overshadowed by imitative research, some of the methological musts that also happen to characterize physical organic chemistry: the devising of experiments so that accurate numerical data can be obtained; the importance of remote, interdisciplinary connections; the need for estrangement from stereotypic preconceptions that may obscure the true explanations for the phenomena; and the over-riding need for concerning oneself only, or at least predominantly, with the important facts that nature tells, if one cares to listen. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: heterogeneous catalysis; organic reactions

INTRODUCTION

Reasons for the estrangement, good or bad

That industrial chemistry has had little influence on academic research in the area of heterogeneous catalysis of organic reactions has both objective and subjective determinants. We shall examine the latter one by one since they are responsible ultimately for the present chasm. In so doing, we shall evoke in passing the attendant underlying reasons for the near-absence of a dialog.

Most often, such communication as exists does not go from chemical industry to chemical science: the information transfer travels in the opposite direction. There is a widespread notion that scientific discovery is the exclusive province of academia, and that it may subsequently lead to industrial applications, that these will 'follow'—both the noun 'applications' and the verb 'to follow' are meaningful here. The same mindset dichotomizes—as indeed, catching the reader unaware, we just did in one of the above statements—chemistry into a science and an industry as two related but separate activities, a division of labor and a segregation that does disservice to both, and that unfortunately tends to underestimate contributions to the science, including fundamental breakthroughs, from the industrial quarter.

Of course, such stereotypes as the academic ivory tower and industrial empiricism are rooted in sociological realities: tenure versus the risk and the reality of an abrupt termination; academic freedom versus mandatory success and the pressing immediacy of set goals; university salaries versus more comfortable incomes.

Also, as a second reason for the lack of better industrial–academic communication, industrial secrecy is a deterrent. Although it is well justified owing to the requirements of patent law, it prevents the quick dissemination of exploratory results that is so essential to the advancement of science, in the competitive context of scientific research. Furthermore, when several years have elapsed until the individual industrial scientist is allowed to communicate his or her results, the initial enthusiasm, inevitably, will have wilted with the passage of time.

One of the referees of this paper wrote, 'The perceptions presented in this section do not agree with this reviewer's view of reality, at least in the US; namely that communication between industry and academia is more active than ever—out of necessity for both. Today's industry with its short-range focus has to rely on academia for fundamental research and science, but then industry plays the predominant role in defining the relevant, fundable areas for the scientific research.' He is right, and I could not agree more. I was right too. To put it in a nutshell: at zero order, there is estrangement between the science and the industry. At first order, the two entertain close collaboration. At second order, industry farms out to academia only topics of marginal or relatively minor interest, such as 'defensive' research, strategic long-term research,….

Correspondence to: P. Laszlo, Laboratoire de Chimie Fine aux Interfaces B6, Université de Liège au Sart-Tilman, B-4000 Liège, Belgium.

The outstanding record of industrial research

The organic chemical industry is unthinkable nowadays without the benefit of heterogeneous catalysis. A full 100% of the new units put into production make use of it. We shall mention here a few of the catalytic processes, both homogeneous and heterogeneous, that industry has implemented. Following the discovery by Sir Geoffrey Wilkinson of the homogeneous enantioselective hydrogenation catalyst that bears his name, Monsanto based on it the industrial production of L-DOPA, the most efficient drug available against Parkinson's disease. Eantioselective catalytic hydrogenation is also the key to preparing both natural and non-natural amino acids, using a variety of transition metals and ligands.[1] The use of carbon dioxide as a feedstock would be a way of recycling this product of automotive and industrial emissions and thus would make a contribution to the slowing down of global warming: Noyori, probably the world leader in the field of enantioselective catalysis,[2,3] has provided promising exploratory experiments on the homogeneous hydrogenation of carbon dioxide into formic acid and derivatives, such as esters and amides.[4]

From the viewpoint of a rational understanding, such examples of homogeneous catalysis are valuable because by and large we know the mechanism of the reaction and of the processes that have been based on it. With heterogeneous catalysis, as a rule 'black magic' is more prevalent. The best catalysts and promoters were discovered empirically and the field has remained, to this day, more an art than a science. It is important to make direct studies of the catalyst in actual operation, *in situ*, rather than relying on extrapolations from a simplified model.[5] A case at hand is the hydrogenation of carbon monoxide on copper-based catalysts: it is not known if the active surface is metal or oxide! As Schögl wrote, 'if the chemical nature of the active species is not known.[6,7] the mechanism of this reaction cannot be worked out scientifically.' He proceeded to show from EXAFS evidence that neither crystalline nor amorphous oxide is present in the catalyst, which consists of metallic atoms.

What are the techniques available at present for studying at atomic resolution the changes undergone by the surface of a catalyst during chemical reaction? Scanning tunneling microscopy and sum frequency generation vibrational spectroscopy are one such technique.[8] Infared imaging is also a non-perturbative technique, offering relatively high spatial resolution and enabling the observation of restructuring and of spatiotemporal patterns in exothermic catalytic surface reactions at atmospheric pressure. It has been applied to the oxidation of carbon monoxide on platinum.[9] Also, gas-phase NMR spectroscopy is well suited to follow the relative kinetics of volatile reaction products over a catalyst and to study competitive adsorption of a number of volatile components over a variety of adsorbents.[10] Transient response techniques also assist the design of gas-phase heterogeneous catalysts.[11]

Arguably, oxidation reactions are the most active sector of heterogeneous catalysis nowadays. We shall mention just a handful of examples. Using vanadium phosphorus oxides, with traces of other compounds, as catalysts, at temperatures of 360–460 °C, at pressures just above ambient and for very short reaction times (a few seconds), *n*-butane is oxidized to maleic anhydride, and subsequently hydrated to the acid prior to catalytic hydrogenation to THF. A 10^8 1b yr^{-1} plant went into operation for Du Pont in the Asturias region of Spain in 1995.[12]

The oxidative coupling of methane to ethane, converted *in situ* into ethylene with 90% selectivity and 40% methane conversion, is an extremely attractive goal (so far unattained) given the enormous proven reserves of natural gas. Likewise, ethylene is by far the largest volume organic chemical: its global production is of the order of 60 Mt yr^{-1}. For this purpose methane is activated on a metal oxide surface—strongly basic oxides that are p-type semiconductors at high temperatures and display oxygen anion mobility, such as magnesia or lanthanum oxide—prior to free-radical chemistry in the gas phase.[13]

OVERVIEW OF OUR WORK

The seminal concept came from prebiotic chemistry. It goes back to J. Desmond Bernal who pointed out, in a lecture in 1945, the numerous assets of clays for the production and protection of the first formed biomolecules. The main advantages that we found in clays for catalysis of organic reactions were the reduction in dimensionality, that ensured ultrafast diffusion of the reactants; the very high Brønsted acidity, that reached routinely surface acidities placing our catalysts between concentrated nitric and sulfuric acids; the ease with which one could modify the clay chemically, by anchoring additional Lewis acidic sites via the surface silanol groups (impregnation) or by taking advantage of the polyelectrolyte character of the anionic silicate sheets to replace the natural counter ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+, etc.) with higher valent metallic ions, such as Fe^{3+} (ion exchange). In this manner we could tailor catalysts to a number of important organic reactions.

The Diels–Alder reaction is well known to be catalyzed by Lewis acids. Doped clays also catalyze it fairly successfully.[14–16] Even 'tough nuts' can be cracked in this manner: with furans as dienes, cycloadditions are normally sluggish on account of the loss of aromaticity between the initial and transition states. Nevertheless, using modified clays as catalysts, reactions could be run at ambient temperature and pressure, instead of requiring 15 kbar of applied pressure for useful yields of reaction products, as the late William G. Dauben had shown.

Another area for catalysis by clays and modified clays

is that of electrophilic aromatic substitution. Nitration of aromatic hydrocarbons such as toluene is performed with high selectivity for mononitration, as opposed to polynitration giving rise to explosive materials, and with high regioselectivity favoring the *para* product, as the late William G. Dauben had also shown.[17]

Likewise, we were able to chlorinate toluene with high selectivity for either ring or side-chain chlorination, making use of zeolite catalysts to direct, through the nature of the outer surface, the silicon-to-aluminum ratio in particular, and the reaction mode either to the radical or the ionic type.[18]

A major reaction in organic chemistry, whether industrial or academic, is the Friedel–Crafts reaction. We teach students, over-enthusiastically, that it is *catalyzed* by Lewis acids such as aluminum chloride. Actually, secondary products such as chloride ions from alkyl or acyl chlorides poison the catalyst through coordination with the vacant p orbital on aluminum. Hence *stoichiometric* rather than catalytic amounts are required. Recourse to Lewis acidic sites in clays, either exchanged or impregnated with Lewis acidic cations, provides extremely efficient catalysis of Friedel–Crafts alkylations[19,20] and acylations[21] with the environmental asset of vastly reduced, by factors of up to 1000, amounts of catalyst as compared with the standard procedures using aluminum chloride. At least one industrial plant takes advantage of this breakthrough, that we pioneered.

We have also designed and implemented heterogeneous catalysts for oxidations under mild conditions. Catalysis of the epoxidation of ethylenic double bonds became an urgent practical problem when the standard reagent *m*-chloroperbenzoic acid (MCPBA) became an outcast owing to the risks in storage and in transportation. Efficient catalysts are derived from phyllosilicates through ion exchange and impregnation by transition metals. Air oxygen serves as the oxidant in the presence of a sacrificial auxiliary.[22]

REMARKS ON METHODOLOGY

Setting-up experiments

Chemistry is a voluntary science: we want to make nature answer our questions. Hence, this self-evident assertion has to be implemented: design the experimental system so that (i) simple questions can be put to it and (ii) answers to these questions can legitimately be expected.

Reproducibility is all-important. The area of heterogeneous catalysis by clays poses two problems in this respect. The first, given the vast diversity of natural clays and the range of variation of composition within each clay type—for instance the amount of iron as an impurity within the montmorillonite family of clays is highly variable, depending on the origin of the sample and even on its location in the mined deposit—is obviously not to use clay dug-up from your garden! For this reason, we relied heavily on industrial clay catalysts, produced in boxcar amounts for the petrochemical industry, with applications such as hydrocarbon cracking. The K10 montmorillonite, manufactured by Süd-Chemie (Munich, Germany) by acid treatment and calcination of a clay from a mine in Bavaria, is a prime example. The second problem, with respect to reproducible results, is control of the moisture level. It is imperative that the clay and the ensuing catalyst be kept at all times either in a dry box or in an oven. If and when the clay powder absorbs humidity above a certain level, it may well become inactivated in an irreversible manner.

A case at hand can be quoted. We had recruited two new co-workers in the Liège group, a team consisting of a post-doctorate worker and of a technician to assist him. For several months, all their results were irreproducible. The origin of the problem was that the former had been trained initially in synthetic organic chemistry and accordingly he was used to working with very small samples. He was preparing the 'clayzic' catalyst (clay-supported zinc chloride) in too small batches of *ca* 10 g in crucibles. As soon as we changed the scale for preparation of the catalyst, boosting it by a factor of 10 to about 100 g, in capsules, the results became reproducible.

Sound experimental design (just like driving a car or living an interesting life) admits to three rules: anticipate, anticipate and anticipate. Try to think up all the parameters that might be relevant to your experiment. The work we did with 'clayzic' provides an illustrative example. A rival group in the UK (that of Dr James H. Clark at the University of York and of Dr Tony W. Bastock at Contract Chemicals) was performing the activation of this catalyst by calcination in air at 280 °C overnight.[23] We were able to perform adequate and similar activation of the catalyst also by calcination overnight in air, but at a much lower temperature (120 °C), less likely to alter the clay structure: we reasoned (and observed) that thin-layering the sample to be thermally activated ensured much greater uniformity of temperature within the sample. Ceramics are made from clays, it should be recalled, and they make excellent thermal and electric insulators.[24,25]

The art of data analysis

Whatever the experimental system under study, one is provided easily with masses of data. In the area of the heterogeneous catalysis of organic reactions, such data consist, typically, of the reaction yield as a function of time; of the rate of reaction as a function of the amount of catalyst; and of the product distribution as a function of time, monitored typically by gas or liquid chromatography. Many other types of data can be and are gathered. My first observation, very mundane but worth restating

since few people take heed of it, is not to undertake an experiment without first making sure that you will be able to come up with a model and with the attendant numerical simulation to analyze the data. The second recommendation is to plan also data collection with a view to data reduction: colleagues in statistics will be helpful in this respect. A good rule of thumb is that, if N parameters are to be extracted from the data and determined reliably, then the minimum number of data points is $3N$. Third, in general one should analyze data using two completely independent methods so that their convergence gives some guarantee as to reliability of the results. Such advice, however trite, also goes unheeded most of the time. Remember that the uncertainties in the results, as the computer spits them out, reflect only random errors. In general, systematic errors are (much) worse. In general, the sources of systematic error are unidentified. Therefore, as an elementary precaution, an estimate of the systematic error should be made lest you delude yourself with the quality of your results: it is actually significantly worse than you think. A good rule of thumb is to multiply the standard deviation of your numerical result by a factor two or three in order to make an estimate of the systematic error, if the experiments have been performed with great care.

In my experience, graphical representation is the most helpful tool in data analysis. The appropriate choice of a plot type, and of the parameters to be plotted can lead to many a discovery. Often, such choices are routine. For instance, in our work on chlorination of substituted toluenes, recourse to a Hammett reactivity–structure plot (as a function of the σ^+ parameter) was obvious.[18] It was less obvious that we would be able to make an inference about the coexistence of two populations of active centers on the catalyst—identified with edge sites and with surface sites on clay platelets—from plotting the product yield as a function of the amount of inhibitor introduced in to the reaction medium.[18]

Clays enriched with metallic ions through exchange or impregnation become outstanding Friedel–Crafts catalysts.[19] This 1987 report[19] was the seed for K10 montmorillonite-impregnated zinc chloride, known as 'clayzic.'[26] The lamb turns into a lion. Somehow, once impregnated on the surface of a solid aluminosilicate, zinc chloride, normally a weak Lewis acid[27] and a poor Friedel–Crafts catalyst,[28] turns upon thermal activation into one of the most effective catalysts for both Friedel–Crafts alkylations[24,29] and acylations. We note here in passing that Liège 'clayzic' is activated at 120 °C only, whereas York 'clayzic' is activated at 280 °C, a higher temperature likely to destroy more of the remaining clay structure.[21] In addition to its high activity, this heterogeneous catalyst, 'clayzic', displays enzyme-like substrate selectivity.[24,30–33] Since the amount of 'clayzic' needed for a Friedel–Crafts reaction is catalytic[29] rather than stoichiometric,[33] it is environment friendly, hence its commercialization as an 'Envirocat' by Contract

Chemicals. On these counts, it is an exciting catalyst, and indeed a few reports have appeared on its properties.[30–40] A recent review article is devoted mostly to 'clayzic.'[23]

Making connections

A simple idea will go a long way. The single example I shall quote is not very original; numerous people have taken a leaf from the album of bio-inorganic chemistry in order to devise efficient new processes. The cytochrome P-450 enzymatic system oxidizes hydrocarbons to make them more hydrophilic and water soluble, and hence more easily excreted. it also converts alkenes into epoxides. The active species is an oxo iron $O=Fe^{IV}$ form. Vanadium oxide (V_2O_5), alone, supported or in combination, is a potent oxidation catalyst, that *inter alia* effects alkane activation. The active centers on the surface of vanadium oxide are $V=O$ double bonds. These vanadium oxo active sites belong to a square pyramid; the four corners of the square are also oxygen atoms. Catalysts such as vanadyl pyrophosphate often operate by oxo transfer, followed by regeneration from an oxidant of the $V=O$ double bond. Nature offers there a firm and compelling analogy. By following it, we were able to devise a novel and efficient procedure for alkene epoxidation with *tert*-butyl hydroperoxide, with selectivities routinely in the range 80–90%.[41]

Cutting to the chase

Ten years ago we devised, among other Lewis acids impregnated on K10 montmorillonite clay, 'clayzic'.[19] Besides Brønsted acidic sites that pre-exist in the highly acidic K10 clay, impregnation supplies additional Lewis acidic sites (Zn^{II}) to the Fe^{III} sites pre-existing also in the clay: a study belabored and confirmed this obvious fact.[34] This new catalyst, 'clayzic', was surprisingly efficient, as indicated above, in Friedel–Crafts alkylations. Thus it became of industrial interest as an environment friendly catalyst because it could be used in catalytic rather than stoichiometric amounts.[20]

This was remarkable, and it hinted that 'clayzic' might display other unusual properties. We looked for them, out of intuition that this inorganic material would display enzyme-like behavior [just like the numerous metalloenzymes based upon zinc(II)]. Indeed, addition of benzene was found to improve significantly the alkylation of a competitive co-reactant such as toluene, mesitylene or *p*-xylene.[24] In addition to such synergism, the presence of a co-reactant can also invert the relative reactivities: whereas toluene was more reactive than mesitylene in separate alkylations, a one-pot reaction favored mesitylene.[31] Likewise, mesitylene was benzoylated faster/slower than anisole in separate/joint reactions.[42] Yet another observation was beguiling: whereas

benzyl chloride is normally more reactive than benzyl alcohol towards aromatic hydrocarbons as Friedel–Crafts substrates, at 20 °C alkylation of toluene is totally inhibited in the presence of an equimolar mixture of the two benzylating agents, with 'clayzic' also present. At 80 °C, all the alcohol molecules were first converted. Then, and only then, 45 min after the onset of the reaction, the chloride molecules started to react in turn.[32]

In other words, 'clayzic' displays an enzyme-like substrate selectivity and this is probably its most noteworthy feature. We did not content ourselves with discovering the remarkable phenomenon, we also looked for the explanation. In the most enigmatic occurrence, that of the apparent partial inactivation of benzyl chloride in the presence of benzl alcohol, we showed that poisoning of the active Zn^{II} centers by the alcohol molecules was responsible and, as befits physical organic chemistry, we determined quantitatively adsorption constants of alcohol molecules and of benzyl chloride on the catalyst.[33,43]

Stultifying preconceptions

The task of physical science is to gain a better understanding of phenomena. There is no better way than to observe them with care, to listen to what nature tells us about itself. To bring to any such study a preformed notion of what the observed phenomenon should consist of is an obvious mistake. I shall mention here a single concept, the lock-and-key model that was introduced first by Emil Fischer to account for the specificity of interaction between an enzyme and its substrate. Such congruence of molecular shapes has become an immensely influential and prolific paradigm. It has spawned subdisciplines that are thriving, such as molecular recognition and the whole part of supramolecular chemistry devoted to inclusion complexes of various types.

However, the concept of the congruence of complementary shapes can also become imperialistic, whenever it is adopted with uncritical enthusiasm. To apply it to zeolite catalysts when the size of the substrate prevents entry into the channels and supercages is a clear self-contradiction, a pitfall into which many an investigator has fallen headlong. The same concept served to justify the synthesis of numerous pillared clays in the hope that the chambers and galleries thus defined would serve as microreactors producing high selectivity. By and large, and despite considerable activity in this field during the last two or three decades, not much has come out of it.[44] We came up against the same kind of prejudice in our work with 'clayzic' True, it is a mesoporous solid and a variety of reliable techniques can determine the average size of the pores. However, the existence of such porosity in the *structure* does not guarantee that it be relevant to *reactivity*, and the logical link has failed to be established.[34,39,45,46]

Leaders and followers

Breakthroughs are aptly named; they become quickly avenues of 'research.' Perhaps the greatest problem in science nowadays, tightly coupled with the bureaucratization of research funding and management (an activity that tends to be performed more and more by science dropouts without enough experience in many years of research at the leading edge), is the crowding out of creative research by imitative research. In this area of heterogeneous catalysis, the effort must go with priority to the design and invention of new catalysts. Their subsequent characterization using all the available routine techniques is a necessity. However, to let it become the only activity in a 'research group' is to condemn such a group to at best an ancillary and rather sterile pursuit.

CONCLUSION

One might define physical organic chemistry not only as a hybrid from organic and physical chemistries but perhaps more accurately as the mindset seeking explanations of organic structure and reactivity, without preconceived notions, through a combination of rationally devised experiments, of recourse to well chosen models, and of the interplay of experiment, spectroscopic observation and theory in building logical strings of testable propositions. Despite hasty conclusions as to its demise at the end of the 1960s, when synthetic organic chemistry came to the fore after physical organic chemistry had exhausted and perhaps to some extent ridiculed itself with the classical–non classical 2-norbornyl cation controversy, the sub-discipline has undergone a renaissance and has, phoenix-like, risen from its ashes. There are many signs of this revival. That a recent issue of *Pure and Applied Chemistry* was devoted to it is one them, with papers devoted *inter alia* to physical organic chemistry applied to materials science,[47] to the ubiquity of physical organic chemistry,[48] or conversely to its relevance to the seemingly arcane topic of carbon–hydrogen bond activation in the gas phase,[49] or even to the continued impact of physical organic chemistry on free-radical chemistry.[50]

I submit that surface chemistry, as exemplified by the heterogeneous catalysis of organic reactions, offers a choice terrain for physical organic concepts and methodologies.

REFERENCES

1. J. Albrecht and U. Nagel. *Agnew. Chem., Int. Ed. Engl.* **35,** 407–409 (1996).
2. R. Noyori. *Asymmetric Catalysis in Organic Synthesis.* Wiley, New York (1994).
3. R. Noyori. *Science* **248,** 1194–1199 (1990).

4. P. G. Jessop, T. Ikariya and R. Noyori. *Chem. Rev.* **95,** 259–272 (1995).

5. R. Schlögl. *Angew. Chem., Int. Ed. Engl.* **32,** 381–383 (1993).

6. G. Ertl. *J. Vac. Sci. Technol. A* 124 (1983).

7. B. S. Clausen. *J. Catal.* **132,** 524 (1991).

8. P. S. Cremer, B. J. McIntyre, M. Salmeron, Y.-R. Shen and G. A. Somorjai. *Catal. Lett.* **34,** 11–18 (1995).

9. S. Y. Yamamoto, C. M. Surko, M. B. Maple and R. K. Pina. *J. Chem. Phys.* **102,** 8614–8625 (1995).

10. P. M. Kating, P. J. Krusic, D. C. Roe and B. E. Smart. *J. Am. Chem. Soc.* **118,** 10000–10001 (1996).

11. P. L. Mills and J. J. Lerou. *Rev. Chem. Eng.* **9,** 1–96 (1993).

12. W. Stadig. *Chem. Process.* (1992).

13. J. H. Lunsford. *Angew. Chem., Int. Ed. Engl.* **34,** 970–980 (1995).

14. P. Laszlo and J. Lucchetti. *Tetrahedron Lett.* **25,** 1567–1570 (1984).

15. P. Laszlo and J. Lucchetti. *Tetrahedron Lett.* **25,** 2147–2150 (1984).

16. P. Laszlo and H. Moison. *Chem. Lett.* 1031–1034 (1989).

17. L. Delaude, P. Laszlo and K. Smith. *Acc. Chem. Res.* **26,** 607–613 (1993).

18. L. Delaude and P. Laszlo. *J. Org. Chem.* **55,** 5260–5269 (1990).

19. P. Laszlo and A. Mathy. *Helv. Chim. Acta* **70,** 577–586 (1987).

20. J. H. Clark, A. P. Kybett, D. J. Macquarrie, S. J. Barlow and P. Landon. *J. Chem. Soc., Chem. Commun.* 1353–1354 (1989).

21. A. Cornélis, A. Gerstmans, P. Laszlo, A. Mathy and I. Zieba. *Catal. Lett.* **6,** 103–110 (1990).

22. P. Laszlo, M. Levart and G. P. Singh. *Tetrahedron Lett.* **32,** 3167–3168 (1991).

23. J. H. Clark, S. R. Cullen, S. J. Barlow and T. W. Bastock. *J. Chem. Soc., Perkin Trans. 2,* 1117–1130 (1994).

24. A. Cornélis, C. Dony, P. Laszlo and K. M. Nsunda. *Tetrahedron Lett.* **32,** 1423–1424 (1991).

25. A. Cornélis, P. Laszlo and S.-F. Wang. *Catal. Lett.* 63–69 (1993).

26. C. M. Brown, S. J. Barlow, D. J. Macquarrie, J. H. Clark and A. P. Kybett. *Eur. Pat* 0 352 878 (1990).

27. P. Laszlo and M. Teston. *J. Am. Chem. Soc.* **112,** 8750–8754 (1990).

28. G. A. Olah. *Friedel–Crafts Chemistry.* Wiley, New York (1973).

29. F. M. Asseid, J. M. Miller and J. H. Clark. *Can. J. Chem.* **70,** 2398–2404 (1992).

30. P. Laszlo and M.-T. Montaufier. *Tetrahedron Lett.* **32,** 15611–564 (1991).

31. A. Cornélis, C. Dony, P. Laszlo and K. M. Nsunda. *Tetrahedron Lett.* **32,** 2901–2902 (1991).

32. A. Cornélis, C. Dony, P. Laszlo and K. M. Nsunda. *Tetrahedron Lett.* **32,** 2903–2904 (1991).

33. P. Laszlo and M. Davister. *Tetrahedron Lett.* **34,** 533–536 (1993).

34. S. Barlow, T. Bastock, J. Clark and S. Cullen. *Tetrahedron Lett.* **34,** 3399–3342 (1993).

35. J. H. Clark, A. P. Kybett, M. J. Darby, S. J. Barlow, P. Landon and K. Martin. *J. Chem. Res.* 74–75 (1991).

36. J. H. Clark, S. R. Cullen, S. J. Barlow and T. W. Bastock. *J. Chem. Soc. Perkin Trans. 2,* 411–414 (1994).

37. S. R. Cullen. DPhil Thesis, University of York (1994).

38. C. N. Rhodes, M. Franks, G. M. B. Parkes and D. R. Brown. *J. Chem. Soc., Chem. Commun.* 804- (1991).

39. C. N. Rhodes and D. R. Brown. *J. Chem Soc., Faraday Trans.* **88,** 2269–2274 (1992).

40. P. D. Clark. *Catal. Lett.* **25,** 163–168 (1994).

41. P. Laszlo, M. Levart, E. Bouhlel, M.-T. Montaufier and G. P. Singh. *Toward Catalysis of Selective Epoxidation and its Applicability to Multistage Organic Synthesis in Catalytic Selective Oxidation* pp. 318–324. American Chemical Society, Washington, DC (1993).

42. P. Laszlo and M.-T. Montaufier. *Tetrahedron Lett.* **32,** 2901–2902 (1991).

43. G. D. Yadav, T. S. Thorat and P. S. Kumbhar. *Tetrahedron Lett.* **34,** 529 (1993).

44. R. Mokaya and W. Jones. *J. Chem. Soc., Chem. Commun.* 929–930 (1994).

45. C. N. Rhodes and D. R. Brown. *J. Chem Soc. Faraday Trans.* **89,** 1387 (1993).

46. S. J. Barlow, T. W. Bastock, J. H. Clark and S. R. Cullen. *J. Chem. Soc., Perkin Trans. 2,* 411–414 (1994).

47. M. Lahav. *Pure Appl. Chem.* **69,** 255–256 (1997).

48. K. N. Houk and J. K. Lee. *Pure Appl. Chem.* **69,** 237–239 (1997).

49. D. Schröder, C. Heinemann, W. Koch and H. Schwarz. *Pure Appl. Chem.* **69,** 273–280 (1997).

50. K. U. Ingold. *Pure Appl. Chem.* **69,** 241–243 (1997).