Article

# Fraud in Organic Chemistry*

Mordecai B. Rubin

**Schulich Faculty of Chemistry, Technion – Israel Institute of Technology, Haifa, Israel**
**(e-mail: *chrubin@tx.technion.ac.il*)**

Dedicated to the Memory of Athel Beckwith

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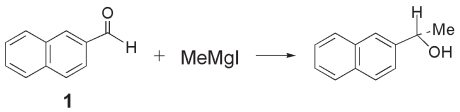
Under the general heading of scientific misconduct there is a classification into fabrication, falsification, and plagiarism (FFP). Fabrication is making up scientific publications out of whole cloth whereas falsification is changing results that already exist so that those reported do not actually represent the research record. The distinction is often unclear and the more general term *fraud* is used here for both kinds of behaviour. Misconduct is also used for lesser evils such as failing to cite the work of others or delaying the return of refereed papers. Plagiarism, using another's intellectual property without giving credit, is a very different phenomenon and is discussed separately.

The prevalence of fraud in the field of organic chemistry has been a topic of long interest. Investigations of fraud by the author include the literature, word of mouth and discussions following a much-presented lecture entitled *Sin in Chemistry*: *Mistakes and Fraud in the Chemical Literature*, as well as some 60 years as a practicing organic chemist.

## Blatant Fraud

Participants in the May 1994 Bürgenstock Stereochemistry Conference (including this author) had the unusual opportunity of witnessing fraud in real time. On arrival, each participant received a reprint of a paper entitled *Enantioselective Reactions in a Static Magnetic Field*.[1] One of the free afternoons of the conference was sacrificed to a presentation of this work by G. Zadel, the doctoral student, advanced to PhD, from the University of Bonn who was mainly responsible for the work. The senior author, Professor Breitmaier, declined the conference invitation on the grounds that his teaching duties made it impossible for him to attend.

The remarkable results included 98% enantioselectivity (either + or -) in the reaction of 2-naphthaldehyde (**1**) with methyl magnesium bromide in a magnetic field of 1 tesla and a number of similarly startling results of Grignard and metal hydride reactions! The speaker gave a good presentation and handled himself well in a vociferous discussion period after his presentation.




**1**

It was revealed in the discussion that at least two other laboratories had tried to reproduce these results and failed to observe any enantioselectivity whatsoever. Workers from one of these had journeyed to Bonn, bringing their own glassware and chemicals and the enantioselectivity was reproduced under Zadel's direction. It was successful with Zadel in Bonn but not elsewhere without him; something was very fishy.

The problem was resolved just a few weeks later when *Angewandte Chemie* published a short paper by Breitmaier entitled *No Enantioselective Reactions in a Static Magnetic Field*.[2] Zadel had admitted that optically active product had been added surreptitiously to the tubes before exposure to magnetic fields and the Grignard reaction. There was no enantioselective reaction at all; the optically active material had been there from the beginning. I felt cheated.

The above example is a clear-cut case of fraud, outstanding in the rapidity of its exposure. The true description of the experiments was not given, the presentation was a lie, and the perpetrator confessed to his actions. The maximum punishment available to universities for serious misconduct such as this is usually revocation of the culprit's degree or loss of his position. The University of Bonn did, in fact, revoke Zadel's DPhil degree. He appealed and his appeal was denied by a lower court in Köln. Ten years after the original paper appeared, a higher court in Münster refused to consider his appeal, effectively terminating the legal struggle to avoid the consequences of his actions.

What could have been the motivation for Zadel's actions? This is a puzzle. Working in an area of considerable current interest[3] where similar experiments of others had given minimal results, he could be certain that his work would be checked and shown to be fraudulent. How could he expect to avoid being shown a charlatan and suffer penalties for his actions?

A considerable number of books on the subject of scientific misconduct have appeared over the years.[4-9] With the exception of the Grayson books that are largely intended to be bibliographic in nature, they recount in more or less detail the story of frauds that have been exposed and comment on the factors involved. There is a good deal of repetition among them and much bemoaning of the present state of science.

## Historic Fraud

The chemical literature in its enormity is the repository of our knowledge of chemistry. Millions of papers combine to provide the information on which chemistry is based. There is an unwritten agreement amongst all chemists that what appears in our published papers is as nearly as possible the whole truth. Deviation from this agreement is a sin against chemistry and the culprit is a sinner who

deserves severe punishment. M. Polanyi wrote :[10]

> *If each scientist set to work every morning with the intention of doing the best bit of safe charlatanry which would just help him into a good post, there would soon exist no effective standards by which such deception could be detected. A community of scientists in which each would act only with an eye to please scientific opinion would find no scientific opinion to please.*

The idea of fraud by scientists has become widespread as evidenced by the publication of novels[11,12] and plays[13] in which scientific fraud is a significant element. There is even a blog on retraction of scientific papers.[14]

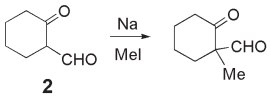
## Fraudulent Papers in Organic Chemistry

Listings of all the cases of fraud detected in organic chemical and related literature by the author over the passing decades appears chronologically below.

**1940:** Goldwasser and Taylor's[15] analysis of hexene mixtures by fractional distillation was checked by Whitmore *et al*.[16] who obtained very different results using identical equipment.

**1943:** Stockstrom's results concerning approaches to the synthesis of Vitamin D were retracted by Dimroth, his supervisor.[17] They were imaginary results existing only on paper and are referred to as *thought* or *Gedanken* experiments.

**1944:** Paranjape and coworkers[18] reported a total synthesis of racemic santonin in 1943 but one year later[18] reported that, upon checking the optical rotation of their synthetic product, they found that it was optically active with an optical rotation close to that of natural santonin. They claimed that the optical activity was introduced in the initial step, the base catalyzed methylation of 2-formylcyclohexanone (**2**). The subsequent steps were reported to lead to total synthesis of the natural, optically active santonin. Cornforth, Cornforth, and Dewar[19] obtained only a racemic (liquid) methylation product when they repeated the base catalyzed step, as would be expected.




**2**

**1957:** Hammond and Ravve[20] reported the reaction of the triphenylmethyl radical with aromatic compounds. The result was corrected by Benkeser, Gosnell, and Schroeder[21] and a subsequent examination by Hammond[22] led to the conclusion that the incorrect results had been fabricated; he blamed himself in part for rushing into print.

**1963:** Benkeser, Grossman, and Stanton reported[23] syntheses of interesting silacyclopentadiene and related compounds over 1961-62. However, a retraction by Benkeser and Stanton appeared within two years[23] as Grossman had fabricated results. Among other things, he took advantage of the fact that the C and H compositions of $C_mH_nSi_p$ are nearly identical to those from $C_mH_nN_{2p}$. The C,H analyses Grossman obtained came from nitrogen compounds that fit the requirement. When Benkeser received the results from the analytical laboratory, they were in agreement with the values calculated for the silicon compound as silicon had not been analysed. The fraud was exposed when other researchers in the laboratory could not repeat Grossman's results. His doctorate degree was revoked by Purdue University.

**1979:** Chatterjee reported work related to the synthesis of aconitine.[24] Cornforth and Pengelly[25] were unable to repeat the first three steps of this work.

**1986:** Breslow and Mehta published three papers[26] reporting turnover rates of catalysis by small molecules that approached the values for enzymes. These were retracted when it was not possible to repeat the results.

**1994:** Zadel's doctoral work[2] in Breitmaier's laboratory has been discussed.

**2006:** A number of papers in synthetic organic chemistry from the Sames group[27] were withdrawn and one paper was corrected[28] with statements that included *the laboratory of the corresponding author (D. Sames) has been unable to reproduce some of the key results*. B. Sezen was found guilty both by the Federal Agency and by Columbia University[29] of fabricating her results.

**2009:** A paper by Gilbert, Fischer and Chen[30] in 2000 on the allyl radical was shown to be a fraud after workers in other laboratories encountered difficulties in reproducing the results. A retraction and a new paper appeared in 2009.[31]

**2009:** Krishna Murthy at the University of Alabama fabricated ten protein structures.[32]

**2010:** An editorial in *Acta Crystallographica* by Harrison, Simpson and Weil[33] reported at least 70 fabricated X-ray crystallographic structures by T. Liu and H. Zhong from Jinggangshan University, China. The Chinese took *bona fide* sets of published X-ray data, replaced one or more of the atoms, made minor adjustments to the structure, and submitted the results to *Acta* as a set of original data for the accompanying *new* structure. They have admitted to 70 such fabrications and more are expected.

Finally, a curious affair in the 1930s in the laboratory of Prof. F. Kögl at the University of Utrecht involved fraud but how and by who has never been clarified. It was examined in detail by Prelog when he was sorting Ruzicka's papers posthumously for the ETH files. He found reports concerning Kögl, Ruzicka's successor at Utrecht, one of which stated that tumour cells contained higher than normal concentrations of D-amino acids;[34] the experimental result could not be repeated. Prelog's summary (in German and available from the author) was concluded by him, stating that *there is good material for a detective novel here!*

## Frequency of Fraud

Fraudulent papers do not advertise themselves. If work appearing in the literature is significant and relevant to the work of others, likely it will be repeated; otherwise it may rest quietly in its fraudulence as if it did not exist

at all. Even if it seems problematic, few would wish to spend the time and effort to examine its probity - it may just be ignored. Not much credit is given for uncovering fraud. There are also small frauds, such as data smoothing to give a better fit to a desired curve, combustion analyses being doctored a bit so that the values for carbon and hydrogen will fall within the acceptable range, a variety of cosmetic changes introduced into papers, *etc*. These are almost impossible to check.

There only appears to be one attempt to estimate the number of frauds in science and this is due to Broad and Wade.[5] In all probability it would have been better left unwritten. Thus, they say that *most of the cases described (here) involve major fraud by which we mean the reporting of an experiment that did not take place. Minor fraud occurs when the experimenter selects or distorts the data from real experiments so as to make them appear smoother or more convincing. We would expect that for every case of major fraud that comes to light a hundred or so go undetected. For each major fraud, perhaps a thousand minor fakeries are perpetrated. The reader can supply his own multiplication factors; ours would indicate that every major case of fraud that becomes public is the representative of some 100,000 others, major and minor combined, that lie concealed in the marshy wastes of the scientific literature*. The authors gave no basis for their numbers but the fraudulent papers in organic chemistry are merely fourteen cases in seventy years! Remarkable! Are there more? Undoubtedly. How many? We have no idea - but almost certainly far fewer than the 1.4 million predicted by Broad and Wade.

One can state with reasonable confidence, therefore, that fraud is not a major problem in organic chemistry. A reason for this, at least in part, is the nature of research in organic chemistry. Experiments are generally well defined and the results easy to characterize by a variety of standard techniques. The chances of fraud being detected are high and the risk is too great a gamble. The results presented here certainly support the idea that fraud is not a major factor in organic chemistry.

Another approach to evaluating fraud has come from Swazey, Anderson and Lewis.[35] They polled 2000 doctoral students and 2000 faculty members in departments of chemistry, civil engineering, microbiology and sociology at the 99 largest graduate departments in the USA. The participants were asked questions principally concerned with exposure to falsification and plagiarism. Some 6- 9% of students and faculty reported direct knowledge of falsification or plagiarism by student or faculty, but it is not known how many of these are in common.

There are far more instances of fraud in the biomedical area. Research grants are considerable, large groups of researchers common, and pressure is applied to gain results that justify funding renewal. Junior staff are often isolated from the real functions of the laboratory and intermediate staff not involved scientifically in productive ways.

## Factors Reducing Public Disclosure

A significant factor comes into play in reducing the publicity attending fraud. It is much less troublesome to expel the culprit quietly from his position and sweep the whole affair under the carpet rather than go through the pain and inconvenience of a procedure against an individual (who may shout loud and long that he is being discriminated against and is innocent of any sin). It is easier for non-tenured staff such as graduate students and postdoctoral fellows to lose their financial support, be told to go elsewhere, and the whole affair forgotten. Moreover, the person exposing a fraud may be subject to considerable criticism by colleagues.[36]

The accepted criterion for fraud is inability of other workers to repeat a given procedure after due diligence. At the very least, one must be careful before making accusations that may affect an individual's life and career. An example given by Prelog[37] describes the banishment of a student from Votocek's laboratory because the glutamic acid that he had synthesized was optically active; he had been instructed to prepare synthetic glutamic acid and it was expected to be racemic. His product was optically active and, therefore, not synthetic. Later, it was shown that racemic glutamic acid has a considerable tendency to undergo spontaneous resolution upon crystallization, but it was too late to reinstate the banished student whose subsequent fate remains unknown. In all probability he had not cheated.

## Legal Treatment of Misconduct in the USA

Much of the scientific and medical research performed in the USA (and increasingly elsewhere) is funded[38] by Federal grants in the form of contracts between the government agency and the institution where the work is to be performed. Misconduct may be a breach of contract and the government may be entitled to recover all or part of the funds allotted. The US Federal government began to take an active interest in how its science money was being spent with regard to questions of fraudulent events in 1981. There were several hearings of cases of scientific misconduct, mainly in the area of biomedical research and, subsequently, laws and procedures were set in place for the legal treatment of scientific misconduct. A detailed guide for ethical scientific behaviour now has been published.[39]

## Plagiarism

Plagiarism, the third of the FFP trio, is very different from the fraud discussed thus far. It has been defined in federal law as *the appropriation of another person's ideas, processes, results or words without giving appropriate credit*. It is usually considered in the context of appropriating someone else's words as if they were one's own. Plagiarism is a special kind of sin, a violation of intellectual property; the expression *intellectual violence* has been used to describe it. One finds the fruits of one's hard-won scientific achievement appearing, perhaps slightly modified, under someone else's name, and often in an obscure journal so as to minimize the possibility of detection - it is never a pleasant experience. The damage to science is minimal since the plagiarist does not introduce anything

new; he simply clutters up the literature with useless material and, presumably, benefits by increasing his list of publications.

Sometimes fate takes a hand in plagiarism, as in the case of S. F. Martin and L. Paquette.[40] A grant application by Martin was rejected by a committee headed by Paquette. Sometime later, Martin received a grant proposal by Paquette for evaluation. Whole sections of the text were identical with parts of Martin's rejected application. A variety of excuses were proffered, including graduate student and postdoctoral interference, but Paquette was found guilty of misconduct and banned from participation in granting committees for ten years. Also, he supposedly agreed with his university to reduce his research group from 40 co-workers to a more modest 20 who he had time to properly supervise.

*Chemical and Engineering News*, among others, periodically carries reports of such cases. One, in 2008, reported[41] more than seventy plagiarized papers over the 2004-2007 period from an Indian professor. What he had hoped to gain from such a number, other than increased probability of detection, is unclear.

At the University of Bremen, a Chinese guest employed his time copying the doctoral theses of his host's group members. He published a series of papers in Chinese, all plagiarized from the doctoral theses.[42] The plagiarism was detected as soon as a paper appeared in an international journal but it was withdrawn only after vigorous protests; it is being expunged from the chemical literature as was Zadel's paper[1] from the on-line issue of *Angewandte Chemie*.

The availability of most of the published literature in chemistry on the Internet and the ability to modify computer files on personal computers has made it technically easy to plagiarize papers. Thus, a paper can be downloaded, appropriate changes made to the title, authors, abstract and first paragraph, and drawings modified at will so that there is a *new* paper ready for submission. However, computer programs are now available that can detect plagiarism. *CrossCheck*, a commercial program developed by iParadigm (Oakland, CA), applies text matching to a large database of published papers. Reportedly, *Nature* is using CrossCheck for screening submitted manuscripts. The same company also has programs (Turnitin) for screening student papers such as essays in English. Machine examination for plagiarism will undoubtedly be improved with time and the scientific journals can be expected increasingly to examine papers for plagiarism upon submission.

## Peer Review – The Defence Mechanism

The peer review system, using anonymous referee(s) to evaluate the suitability of articles submitted for publication, was begun in the 19th century or earlier by *Nature* and the *British Medical Journal*;[43] it is standard practice today.[44] Undoubtedly, it has contributed enormously to maintaining standards in published papers. Occasionally, referees hide behind their anonymity to make things excessively difficult. J. D Dunitz reportedly found an unsigned referee's report on Mendeleev's paper in a deserted laboratory at the ETH. It stated:

> *This paper is just a rehash of a lot of known facts and contains nothing new. In the unlikely event that it should be published, the table should be omitted since it takes up a lot of space.*

An entertaining example of a referee carrying things to an extreme!

Chemists and scientists in general do not think in terms of fraud when reading a paper. They assume that, while authors may make mistakes, they don't cheat. Considering the small number of fraudulent papers in organic chemistry, this is a pretty good assumption.

Peter Golitz, the talented editor of *Angewandte Chemie*, published a report[45]in 1994 on the sequence of events in the publication of the Zadel paper that opened this article. The paper was sent to three referees. Ref. *A* said it was not worth publishing and should be rejected immediately, *B* said it described a very significant breakthrough and should be published at once, while *C* recommended that further work be done before it was considered for publication. An editor's dilemmas - publish garbage or not publish a breakthrough paper! Further work was done, *A* and *B* did not change their opinions but *C* did, and the paper appeared in *Angewandte Chemie*. Fortunately, only a few weeks passed before the fraud was exposed but two papers describing unsuccessful efforts to repeat the published work had already appeared in the journal.[46]

A classic example of not publishing a breakthrough paper is Beluzov's work on oscillating reactions[47] where a reacting solution oscillates between two different colours as the reaction proceeds. The work was rejected twice because it was *theoretically impossible*. Impossible or not, a Gordon Conference is now held on the subject every summer!

We cannot know how many fraudulent papers have been caught by the refereeing system, since such papers would not be published and nothing would be known about the attempts to have them accepted for publication. We cannot expect referees to spot every blemish of a submitted article, particularly if it is fraudulent.

## Conclusions

The research supervisor can do a great deal to minimize the possibility of fraud. Firstly, research groups should be maintained at a size such that the 'boss' has sufficient time available to give some attention to every co-worker. Secondly, co-workers should understand the objectives of their work without ever feeling that it is incumbent upon them to get a certain result. Pressure of this sort is asking for trouble, especially with a weak personality. One of the invariable excuses of someone caught in fraud is that he was under extreme pressure to get results – and fabrication (or falsification) provided a quick solution.

The best strategy to reduce fraud to the absolute minimum has to be the education of future generations of chemists on the subject, both from the idealistic and practical points of view. The US National Science Foundation and

National Institutes of Health have mandated a course in scientific ethics as a condition of their awards of training grants for graduate students.[48] Such a course has to be a valuable tool in having students think about the general aspects of their chosen career and how they should, and would, behave in a variety of situations including their conduct in research.

Finally, for those interested, an E-mail address is now available to exchange information on scientific fraud: SCIFRAUD@UACSC2.ALBANY.ED

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