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Aqueous Humour - The Art of the Chemical Spoof

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Abstract: Chemical journals are serious things. However, occasionally the humour of chemistry breaks through and hoax or spoof articles are published. This article looks at some notable examples of this human side of our science.

Keywords: Chemistry · Hoax · Spoof

Chemistry is a serious subject. We are taught this from our earliest lessons at school. However, chemists are also human and it is not surprising that there is an established sub-genre of our science in which chemists take themselves a little less seriously. This article brings some classical chemical spoofs to the attention of the community. Please note that the article is concerned with chemical spoofs, designed to amuse or poke fun at the chemical theories, and not fake articles designed to mislead the scientific community. I hope you enjoy these as much as I do.

Let us begin in the first half of the 19th Century CE. Wöhler and Liebig were championing a theory of organic chemistry based on radicals – groups of atoms which persisted unchanged throughout chemical reactions (such as phenyl, ethyl, benzyl, etc.).

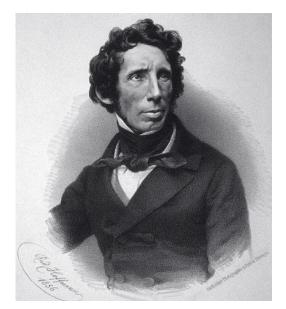


Fig. 1. Friedrich Wöhler (1800–1882), the author of the paper accredited to 'S. C. H. Windler', lithograph by Rudolf Hoffmann, 1856, after a photograph by Petri. Public domain image from https://upload.wikimedia.org/wikipedia/commons/3/32/Friedrich_Wöhler_Litho.jpg

In contrast, Dumas, was an advocate for the theory of types which allowed substitution (for example, $CH_3 \rightarrow CH_2Cl \rightarrow$ $CHCl_2 \rightarrow CCl_3$). Friedrich Wöhler (Fig. 1) wrote a spoof article on substitution reactions which he sent privately to Liebig and Berzelius. Liebig decided to publish the article in Annalen, and it subsequently appeared in 1840 under the title 'Ueber Das Substitutionsgesetz Und Die Theorie Der Typen' (On the Substitution Law and the Theory of Types) and was published under the name of S. C. H. Windler.[1] Wöhler described how he sequentially replaced hydrogen, oxygen, carbon and manganese atoms in manganese(II) acetate (formulated, MnO + C₄H₆O₂) with chlorine, initially producing manganese(II) trichloroacetate and finally, Cl₂Cl₂ + Cl₈Cl₆Cl₆. The compound Cl₂₄ was a yellow solid that closely resembled the original manganese(II) acetate, stating that because "hydrogen, manganese, and oxygen may be replaced by chlorine, there is nothing surprising in this substitution". He makes a claim to novelty with the comment "I believe, however, that atom-for-atom substitution of carbon by chlorine is my own discovery". In a footnote, he adds "I have just learned that there is already in the London shops a cloth of chlorine thread, which is very much sought after and preferred above all others for night caps, underwear, etc." A clever and enjoyable parody which maintains a misplaced scientific logic at its heart.

Surely our Swiss chemists would not indulge in such frivolity? Actually, yes they have! Apparently, Albert Eschenmoser presented a lecture series in Haifa, Israel in 1969 in which he discussed the synthesis of the hydrocarbon (CH)₂₄ and identified conformers which he named helvetane and israelane (Fig. 2). He noted that helvetane was more stable than israelane, The world-renowned chemist David Ginsburg attended this lecture series and was not convinced whether the greater stability of helvetane was "chemical rather than economic". In a masterful parody, published under the name G. Dinsburg and received on 1st April 1982, he discusses the chemistry in detail including the comment on Eschenmoser's synthetic strategy "all reactions are carried out in ordinary round bottom flasks". [2] The April issues of *Nachrichten aus Chemie, Technik und Laboratorium* are always worth looking at as they have contained numerous, excellent parodies over the past three quarters of a century.

Another classical example of an initially convincing publication is found in the 1981 paper entitled 'The generation of a high-





helvetane

israelane

Fig. 2. The two conformers of the hydrocarbon (CH) $_{24}$ identified by Eschenmoser and named helvetane and israelane. The origin of the names is probably obvious!

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ly reactive intermediate in the high temperature pyrolysis of tetramethylsilane' by Dietmar Seyferth and James Pudvin which appeared in the respected ACS journal CHEMTECH.[3] This paper, written in a scientific style which easily fools the casual reader, describes the isolation of 0.2304 g of an amber liquid from the pyrolysis of 6.81 kg of tetramethylsilane at 2250 \pm 20 °C. This liquid exhibited no signals in its ¹H, ¹³C or ²⁹Si NMR spectra. However, a solution in CCl₄ reacted rapidly with water with consequent hydrolysis of the CCl₄. In contrast, chlorination of the solid residue from the pyrolysis of Me₄Si, yielded SiCl₄ that was extremely resistant to hydrolysis. These observations were clarified by the identification of the amber liquid as pure 3d atomic orbitals (Fig. 3). Addition of catalytic amounts of the 3d orbitals to the CCl₄ provided a mechanistic pathway for attack by nucleophiles, whereas the d orbital depleted silicon in the SiCl, had no pathway available for facile hydrolysis. In addition to calculating that the yield of the d orbitals was nearly quantitative and using them as reagents for the synthesis of Me₅N, the authors speculate that it might be possible to generate "pure d_{xy} or pure d_{zz} orbitals". or p_z orbitals by "pyrolytic orbital stripping" of trimethylborane" or f orbitals from "pyrolysis of a suitable lanthanide or actinide organometallic derivative".

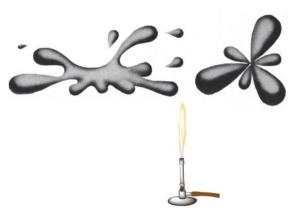


Fig. 3. Two of Seyferth's pyrolysed d-orbitals from the publication 'The generation of a highly reactive intermediate in the high temperature pyrolysis of tetramethylsilane'. [3] (Modified from the original article).

One of my favourite spoof articles is Asimov's 'The Endochronic Properties of Resublimated Thiotimoline' which draws upon his own chemical background and was published in Astounding Science Fiction in 1948, a journal which, at that time, mixed fiction with serious science articles.[4] Asimov starts with the scientifically correct statement "...the solubility of organic compounds in polar solvents such as water is enhanced by the presence upon the hydrocarbon nucleus of hydrophilic -i.e. water-loving groups, such as the hydroxy (-OH) ... group". He then crosses from fact (thermodynamics and solubility) to fiction by correlating solubilty with kinetics (the rate of solution) and makes the observation that the more hydroxy groups in a compound, the faster it appears to dissolve in water. Asimov then introduces the reader to the compound thiotimoline which possesses "at least fourteen hydroxy groups, two amino groups and one sulfonic acid group" which is so soluble (thermodynamics) that it dissolves before the water is added. The remainder of the paper describes detailed physicochemical studies of this phenomenon! The references, all spurious, include an article entitled 'Determinism and free-will. The application of thiotimoline solubility to Marxian dialectic'. Thiotimoline has subsequently found applications in computer technology^[5,6] and has its own entry in Wikipedia! The Spanish version of the Wikipedia article even includes a structure for thiotimoline (Fig. 4) with the caveat to the reader "A possible structure for thiothymoline, as described by Asimov. This compound, of course, would not show the property described by the author if synthesised".

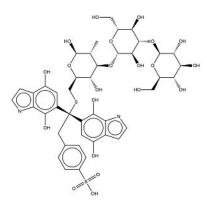


Fig. 4. A possible structure for thiotimoline (that would not have the expected endochronic properties!). Taken from https://es.wikipedia.org/wiki/Tiotimolina.

Nomenclature and structural formulae offer a limitless play-ground for the frivolous-minded, in particular in the context of organic chemistry. However, this is not the place to discuss the anthropomorphic molecules designed and named according to their appearance. The use and abuse of established nomenclature is often the butt of humour and I conclude this paragraph, by noting that although the 'serious' literature contains numerous papers on the aromaticity of arsoles, few authors overstep the bounds of propriety and decency in their publications! Nickon and Silversmith have written an excellent monograph on the topic of frivolous nomenclature in organic chemistry.^[7]

The individuals who are responsible for scientific advances are fair game to the parodist, and one of the lesser known scientific giants is Claude Émile Jean-Baptiste Litre, a manufacturer of wine bottles who ultimately donated his name to the S.I. unit of the litre.[8] Litre also made chemical glassware and it is noted that he donated a set of graduated cylinders to the Royal Society of Edinburgh in 1765, although these were unfortunately subsequently destroyed in the course of Sir Humphrey Davy's preparation of nitrogen trichloride. Apparently, the honouring of Litre in the S.I. unit was at the suggestion of Antoine de Fourcroy. This outstanding fake biography fooled IUPAC who published it in Chemistry International and subsequently printed a somewhat embarrassed apology! A similar false biography has recently appeared as a miscommunication in the Journal of Immaterial Science documenting the contributions of Don Jalton to the development of the atomic model and his early arrangement of elements into a periodic table. [9] The authors comment "His life was a model of the modern-day creed for tourism – Take only memories, leave only footprints. In his case, he left neither memories of his achievements nor footprints in history. We hope that this article redresses that imbalance."

A final area in which the chemist can evoke humour is in the list of authors on a paper. I strongly suspect that at least one of the authors on the 1973 paper entitled 'Photoelectron spectra of phosphabenzene, arsabenzene, and stibabenzene' may have been added as a wry comment on the proliferation of contributing authors. [10] The expression "Uncle Tom Cobley" comes from a folk song and is used in English to express exasperation at a large of people in a list: the chorus ends "Bill Brewer, Jan Stewer, Peter Gurney, Peter Davy, Dan'l Whiddon, Harry Hawke, Old Uncle Tom Cobley and all."

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