

ON SABATIER'S MISREPRESENTATION OF BERTHELOT'S HYDROGENATION OF BENZENE WITH CONCENTRATED HYDROIODIC ACID

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Abstract

Paul Sabatier's attractive story of how Berthelot obtained methyl-cyclopentane in the HI-reduction of benzene, instead of the expected cyclohexane, turns out, upon checking the original literature, to essentially misrepresent what actually happened. How the story unfolded is sketched here.

Introduction

In 1912 Paul Sabatier received the Nobel Prize in Chemistry for his method of hydrogenating organic molecules in the presence of finely divided metals. In his Nobel Lecture he referred to the work of his former Ph.D. adviser Marcellin Berthelot relating to the hydrogenation of benzene with concentrated hydroiodic acid, a method pioneered by Berthelot in the late 1860s, making three points: (i) that this hydrogenation agent was very powerful, (ii) that the experiments were very dangerous to the chemist, in that the hydrogenations were carried out in sealed tubes at 275 °C, so that pressures of over 100 atmospheres may be generated (both from the water, and from the hydrogen formed through the decomposition of HI), often leading to bursting of the tubes with "all too frequent" terrible consequences, and (iii) that the presence of concentrated hydroiodic acid often causes isomerization of the reduced substance, specifically that Berthelot, using benzene, did not get cyclohexane,

"which he had expected," but methyl-cyclopentane (1). This story was of course an excellent introduction to his own catalytic method, which was even more powerful, easy to carry out, and did convert benzene completely into cyclohexane (*e.g.*, sending a gaseous mixture benzene/H₂ through a tube containing reduced Ni at 180 °C and at atmospheric pressure).

This representation of Berthelot's work was repeated, in very similar terms, on various occasions, when Sabatier looked back on his way into catalysis, always emphasizing that the hydrogenation of the aromatic nucleus, and especially benzene itself, was the big challenge (2). Other people also retold the story, *e.g.* his collaborator Alphonse Mailhe (3), and later Armand Lattes (4), and Bert Weckhuysen (5). In his scientific papers and book, however, things are different. In the first, 1901, presentation of their catalytic method, Sabatier and Senderens describe only the details of the method, without any mention of Berthelot's work (6); indeed, there are no references whatsoever (7). Later that year, in a paper describing the catalytic hydrogenation of more complex molecules, containing at least one aromatic nucleus, there *are* references to Berthelot's work, but these mentions are restricted to cases in which the products of the catalytic and the HI routes are identical (8). In his 1913 book *La Catalyse en Chimie Organique* (2nd edition, 1920), Sabatier writes about "the great difficulty of directly hydrogenating the aromatic nucleus," and mentions the reduction of benzene by the HI-method, but without

naming Berthelot, only saying that this method did not produce “cyclohexane, as was *hoped* (“*qu'on pouvait espérer*”), but its isomer, methyl-pentamethylene [i.e. methyl-cyclopentane], which is formed by a molecular rearrangement.” (Translation by E. Emmet Reid, our italics) (9). For this statement Sabatier refers the reader to a 1897 paper by Nikolai Kijner (also written Kishner or Kizhner) (10), rather than to anything Berthelot had written on the subject.

Strange. In fact, Sabatier’s story becomes really suspect once one realizes that Berthelot did not subscribe to the Kekulé structure of benzene (proposed in 1865, and already more or less mainstream a few years later), or any other ring structure for that matter, and so he would not have had any reason at all to expect cyclohexane as the end-product of the reduction of benzene, and indeed he did not, as we will see shortly. Curiously enough, tracing back the story from the Kijner paper referenced by Sabatier, one finds that it looks entirely different from the one presented by him in his Nobel Lecture and subsequent memoirs.

Increasing Insight: How Methyl-cyclopentane Came to be Defined as the Prime Reaction Product (11)

The story does start of course with Berthelot’s work on the reduction of aromatic compounds with concentrated solutions of HI, described in detail in a series of papers published in 1868-69 (standard conditions: sealed glass tubes, 275 °C, 10 h) (12). In the section on the hydrogenation of benzene (13) he does not mention any expectation, and certainly not any *hope*, that cyclohexane (or hexamethylene, as it was then called) would be the reaction product. Indeed, he was interested to see whether he could hydrogenate benzene to its fully hydrogenated counterpart, which in his view, based on his picture of benzene as triacetylene, would be *n*-hexane (see further below)—which in fact was the product obtained after pushing the reaction a bit, and Berthelot was duly gratified. By the way, products were in those days identified by elemental analysis, boiling point, density, and often also refractive index and/or specific reactions (*e.g.*, benzene would react with a 50/50 mixture of sulfuric acid and fuming nitric acid, while a paraffin would not)—this after a bunch of (fractional) distillations to isolate products in as pure a state as possible (14).

Adolf Baeyer had already heard about this method early in 1867, and immediately set about repeating it, but could not initially make it work, as he reported in a

lecture abstracted in the first volume of the *Berichte* (15): he believes that the reduction will not lead to opening of the benzene ring, and ascribes Berthelot’s finding to thermal decomposition of the hydrogenation product (he appears to think that Berthelot applies temperatures as high as 400 °C!, and he uses, moreover, anhydrous HI, rather than a concentrated aqueous solution). Berthelot, in his turn, reacts to this in print (16) by (i) complaining about scientists (naming Baeyer and Graebe) trying to duplicate experiments which they know about only by hear-say, without enquiring into the correct procedure, and (ii) emphasizing again the precise reaction conditions that will lead to the “complete” hydrogenation of benzene, to *n*-hexane that is (silently increasing the reaction time from 10 to 24 hr, and the temperature from 275 to 280 °C). And sure enough, Baeyer now succeeded in replicating the Berthelot experiment, and he writes to tell him so, which Berthelot gratefully acknowledges in a footnote in his next paper on the subject (17). Baeyer reports this finding also in a 1870 paper on another reducing agent, phosphonium iodide (PH₄I), which he expected to be a better performer, but which proved to be unable to reduce benzene to any extent (18).

The matter did not rest there, however. The Russian scientist F. Wreden (St. Petersburg), in the course of a study of camphoric acid, became interested in Berthelot’s reduction method, and started wondering how the closed ring structure in benzene (note that although the exact structure of benzene continued to be debated at the time, it was quite generally accepted that it was some sort of ring structure) could be opened by this method, without then destroying the *n*-hexane formed. After a first skirmish about the correct reaction conditions (again!) between Wreden and Berthelot (19), the former reports in 1877 (20) that in his hands, employing the conditions prescribed by Berthelot (conc. HI, 280 °C, 50 h) the method did not succeed in adding more than 6 H to a molecule of benzene (or toluene, xylene, or isopropyl-toluene, for that matter). Wreden does not enter into the question of the structure of hexahydro-benzene, perhaps assuming that it has to be hexamethylene (cyclohexane), citing a paper by Graebe that would make such an assumption rather plausible (21), only noting that its relatively high density corroborates the conclusion that the ring structure has remained intact (see later August Horstmann (22)). Berthelot took umbrage at this conclusion, of course, and published a rebuttal in the grand style (23), arguing that if a theory predicts that in benzene hydrogenation under forcing conditions the conversion C₆H₁₂ → C₆H₁₄ (modern notation: Berthelot still adhered to the C = 6 system, and would write benzene as C¹²H⁶) cannot take

place, that theory must be wrong, and that everything can be easily understood on the basis of his own theory of relative saturations. That is, since he had shown that it could be synthesized through the condensation of acetylene, $3 \text{C}_2\text{H}_2 \rightarrow \text{C}_6\text{H}_6$, (24) benzene could be thought to consist of a fundamental acetylene molecule, saturated by two other acetylene molecules: $\text{C}_6\text{H}_6 = \text{C}_2\text{H}_2(\text{C}_2\text{H}_2)[\text{C}_2\text{H}_2]$ —in this picture, the hydrogenation of acetylene could be written as:



and the successive hydrogenation products of benzene as:



with no break between hexahydro-benzene and *n*-hexane. A nice piece of paper chemistry, in the usual 19th-century manner, albeit somewhat idiosyncratic (cf. Ursula Klein (25)). Berthelot then showed that in fact, upon repeating the reduction process a few times, one duly gets C_6H_{14} as the end-product of the reduction. That this time the reduction of benzene appears to be more difficult than in his lab 10 years before, Berthelot ascribes, with a bit of hand-waving, to slight differences in the reaction conditions, emphasizing the main conclusion that the hydrogenation moves without breaks from one product to the next, ending with the “absolutely saturated” one, hexane. Thus, while it is not denied that intermediate products exist, they are declared to be relatively uninteresting.

Before discussing the work of N. Kijner, who finally solved the problem of identifying the product of the HI-reduction of benzene, it is appropriate to discuss an 1894 paper by Baeyer first (26). In this paper, “On the constitution of benzene (Part IX),” Baeyer does not report any new experiments relating to the HI-reduction method, but observes (i) that recently Kijner had taken up the subject again, deducing from preliminary reports of his work (27) that the reduction of benzene may not necessarily go as far as hexane, but could give hexahydro-benzene as the major product, (ii) that he himself had reproduced Berthelot’s result, back in 1870, and that he now believed that the ring opening was due to the “simultaneous action of iodine,” and (iii) that even if pure hexahydro-benzene could be synthesized using the HI-method, that method was really not a suitable one, given its “cumbrous-

ness and expensiveness.” And so, Baeyer proceeded to synthesize hexahydro-benzene (i.e., cyclohexane here) starting from tetrahydro-quinone (diketo-hexamethylene, cyclohexane-dione) in a multi-step pathway. In the present context, two results are of particular importance: (a) the boiling point of cyclohexane is 79 °C, while the boiling point of *n*-hexane is 69 °C (which means, says Baeyer, that he and Berthelot did indeed get hexane as the ultimate product—see further below), and (b) that the ring opening is accompanied by a change in heat of combustion and boiling point that differs widely from the changes observed in going from dihydro- to tetrahydro- to hexahydro-benzene. A similar conclusion had been reached by A. Horstmann in 1888 (22), who noted that changes in molecular volume indicated ring closure upon going from heptane to hexahydro-toluene, while further dehydrogenation of toluene left the ring-structure intact.

Kijner carried out his research in V. V. Markovnikov’s lab at Moscow University. In the mid-1880s Markovnikov started his work on Caucasian (Baku) petroleum, when an industrialist provided him with money and samples to investigate Caucasian naphtha products, which at that time started to make their mark on the international market (and, in fact, Sabatier and Senderens referred to them in their 1901 paper). It turned out that these products were rich in aliphatic ring structures, for which Markovnikov coined the term naphtha. To facilitate the analysis (identification) of the many, many components in these naphtha fractions, Markovnikov also started a program to synthesize particular model compounds, inter alia (substituted) hexa- and penta-methylenes (28).

In those days chemists could still write in their papers that they hoped to be allowed to pursue a certain special subject in relative tranquility, and be heeded—in this case it was not to be. True, with some people it did work: for instance, Ossian Aschan, working in Helsingfors (Helsinki; Russian since 1809), announced, after some prodding (29), in his second contribution to the field of Baku oil analysis to leave the rest to Markovnikov (30). And although he subsequently returned to it twice in print (31), he essentially kept his word. With N. D. Zelinsky, however, it was an entirely different matter. Zelinsky, who in 1893 had joined the same laboratory as the one in which Markovnikov was working, proceeded to invade this very area, much to Markovnikov’s chagrin: the latter, and Kijner too, even accused Zelinsky of publishing results he had previously heard about in laboratory meetings in the Moscow institute (32). Markovnikov’s position was weak, however, not fitting at all well into the new organizational structure of the Russian universities

decreed by Konstantin Pobedonostsev in 1881 (the year Tsar Alexander III, whose advisor he was, ascended the Russian throne). This culminated in a conflict which led to his being pensioned off in 1897 (a bit short of his sixtieth birthday) and losing his official residence, too. Luckily, if one may be allowed to use this word in the present context, he was allowed the continued use of the large room which he had fitted up as a private laboratory at an earlier renovation of the institute (28).

Anyway, it was Kijner, working under Markovnikov, who finally identified the product of the HI-reduction of benzene as methyl-cyclopentane (MCP) (10). In his preliminary work he did also obtain hexane as one of the reaction products, but reported that normally one gets almost exclusively a product that can be shown to be MCP. He acknowledges that one might have expected the product to be cyclohexane, but a comparison with Baeyer's data shows that cyclohexane was certainly not the product. In his definitive paper, he applied the original Berthelot conditions (conc. HI [spec. weight 1.96], 280 °C, ca. 24 h), and obtained, almost exclusively, a material, which he calls "hexahydro-benzene" for the time being, of the composition C_6H_{12} , which boils at 71-73 °C (cyclohexane boils at 81-82 °C in his hands, while Markovnikov's synthetic MCP boils at 71-72 °C), and whose density is lower than that of synthetic cyclohexane (Zelinsky). Although *n*-hexane also boils near 70 °C, its composition and density are measurably different from those pertaining to MCP. Nevertheless, to prove beyond any doubt that the compound obtained is MCP, the product was subjected to a number of specific reactions:

1. His hexahydro-benzene dissolves completely in fuming nitric acid—one indeed needs to cool the reaction mixture to avoid accidents—while hexane, and also cyclohexane in the cold (Baeyer, Zelinsky), are inert. He notes, by the way, that this is in contrast to Wreden's report that his hexahydro-benzene is only very slowly attacked by fuming nitric acid, with nitrobenzene as the product...

2. Distillation of the solution resulting from the above reaction (point 1) gave a distillate containing acetic acid, identified by smell and, after a few working-up steps, by a colour reaction with iron chloride (it becomes cherry red). The residue was worked up as well, and led to the isolation of a silver salt, which was suggested, on the basis of the silver content, to be a salt of glutaric acid, $AgOOC-(CH_2)_3-COOAg$. The formation of acetic acid is taken to imply that the hexahydro-benzene contains a methyl-group, and the formation of glutaric acid is pointing to a five-membered ring, rather than a six-

membered one (with would give adipic acid (33)). Also, the milder nitration method discussed below led to a crystalline acid, whose zinc salt is less soluble at higher temperatures than at lower ones, a behavior shown as well by zinc glutarate, which is taken to support the previous conclusion.

3. Mikhail Konovalov, also working with Markovnikov, had developed an elegant nitration method, employing diluted nitric acid, with which cyclic amines became accessible (34). This method could also be applied to further characterize hexahydro-benzene. Indeed, reacting the latter with 12.7% nitric acid led to a tertiary nitro-product, which is only consistent with hexahydro-benzene being MCP. It is to be noted that some degradation of MCP to acidic products takes place (see above, point 2), and also some nitrobenzene is formed (!), which is presumably what also happened in Wreden's case (see above, point 1).

Having established, with "sufficient certainty," that his hexahydro-benzene is indeed MCP, Kijner addresses the question whether the HI-reduction of benzene leads *only* to MCP, or also simultaneously to cyclohexane (hexamethylene). He opts for the second alternative, because repeated fractional distillation always resulted in a minor fraction that boiled at a higher temperature than MCP. As the boiling point of this fraction appears to be near 80 °C, it is natural to conclude that it must be cyclohexane. The ultimate question regarding the mechanism of the conversion of benzene into MCP remains. The reduction does not go to cyclohexane first, followed by its isomerization to MCP, as HI is without effect on cyclohexane itself (35), implying that cyclohexane and MCP are formed in parallel: this means that Sabatier's remark in his Nobel Lecture that HI induces an isomerization reaction is, as such, not true either. Although it had been found that conversion of substituted cyclo-hexanes does often lead to cyclo-pentane derivatives (36), a fact explained by Baeyer's ring-strain hypothesis, its detailed mechanism also remained obscure. Interestingly, cyclohexyl iodide is converted to MCP in HI at 230 °C, and Markovnikov (37) notes that also some cyclohexane, and even *n*-hexane is co-produced. Although this points to the conditions in which ring-contraction can take place, no attempt at a more precise description of the ring-opening and -closure reactions was made.

That HI is not able to catalyze the isomerization of cyclohexane is, of course, in agreement with modern ideas about the effectiveness of strong acids (38). Later it was found that the Friedel-Crafts catalyst $AlCl_3$ could do the trick. After a first mention by Aschan (1902) (31),

the world had to wait to the early 1930s before Costin D. Nenitzescu and collaborators (39) clarified the conditions under which the reaction occurs (one of the “tricks” is to add the now well-known co-catalyst water: experiments with water-free aluminum chloride failed to give any conversion of cyclohexane), and also showed that cyclohexane \rightleftharpoons MCP is an equilibrium reaction (the equilibrium can be approached both from the cyclohexane and from the MCP side). Remarkably, Nenitzescu also wrote that he be allowed to work on this subject in tranquility, and then came into collision with Zelinsky, but this time the latter was the complainer, charging the former with not acknowledging his priority, which Nenitzescu could rebut quite easily, having discussed Zelinsky’s obscure 1898 paper (only in Russian) in one of his first papers on the subject (40)!

Conclusion: How Could Sabatier Get it Wrong?

As we have seen, Berthelot’s HI-reduction method, presented in 1868-69, proved to be a relatively popular tool, but Sabatier misrepresented the results Berthelot obtained himself with it in the reduction of benzene: he did not only not expect to get cyclohexane, but he also, at least as far as he was concerned, did not obtain methyl-cyclopentane either, but hexane, in his eyes the natural final hydrogenation product. Subsequently, various chemists, who accepted a ring structure for benzene, revisited this work, and they did wonder how the benzene ring could open and, when MCP emerged as the major product, then could close again. Curiously enough, in the course of time, it became more and more difficult to “complete” the reduction and obtain hexane, even in Berthelot’s own hands, and indeed in the final paper on the subject, Kijner’s, Berthelot’s original reaction conditions led to almost pure MCP. It was also shown that the reaction does not go via cyclohexane, as the isomerization of cyclohexane to MCP is not catalyzed by HI (and also not by I₂, presumably (41)).

The question remains, then, how Sabatier could get it wrong. Perhaps the facts that (i) *n*-hexane and MCP turned out to have almost the same boiling point, and (ii) Kijner obtained MCP applying the original Berthelot recipe, suggested to Sabatier, that Berthelot probably had obtained MCP as well—indeed, Markovnikov also inclined to this view (42)! If so, this would still disregard Berthelot’s elemental analysis, showing his product to be C₆H₁₄, the absence of any surprise on Berthelot’s part, and the fact that Baeyer, and to a certain extent

also Kijner, did find hexane as the product, or one of the products, of the HI-reduction of benzene. Nevertheless, it certainly seems possible that in constructing a nice story leading up to his own discovery, Sabatier imagined Berthelot’s work with too large a dose of hindsight. But all this must remain, of course, speculation. It would be nice to know, though, whether anybody has ever looked up the original literature, and then tried to make Sabatier see the errors of his view... After World War II this pre-history faded from view anyway, if Hilton A. Smith’s 1957 overview on the catalytic hydrogenation of aromatic compounds is anything to go by: its first sentence goes, “The study of the addition of hydrogen to organic compounds received little attention prior to the twentieth century,” and that’s all he has to say about that period, Sabatier and Senderens’ method having carried all before it (43). Nevertheless, the present paper nicely illustrates how developments in catalytic chemistry and structural organic chemistry became intertwined in the decades around 1900 (44).

References and Notes

1. P. Sabatier, “The Method of Direct Hydrogenation by Catalysis,” Nobel Lecture, 11 December 1912, <https://www.nobelprize.org/prizes/chemistry/1912/sabatier/lecture/> (accessed May 12, 2021). Sabatier’s doctoral project with Berthelot was not concerned with organic, but rather with inorganic chemistry, *viz.* on the synthesis and properties of metal sulfides, leading in 1880 to a doctoral thesis, entitled *Recherches thermiques sur les sulfures*. (See further, *e.g.*, Ref. 4.)
2. P. Sabatier, “Hydrogénations et déshydrogénations par catalyse,” *Ber. Dtsch. Chem. Ges.*, **1911**, *44*, 1984-2001. P. Sabatier, “How I Have Been Led to the Direct Hydrogenation Method by Metallic Catalysts,” *Ind. Eng. Chem.*, **1926**, *18*, 1005-1008. P. Sabatier, “Les Hydrogénations Directes sur le Nickel,” *Bull. Soc. Chim. Fr., Mémoires*, *5e Sér.*, **1939**, *6*, 1261-1268.
3. A. Mailhe, “Paul Sabatier,” *Chemiker-Zeitung*, **1912**, *Nr. 149*, 1451-1452.
4. A. Lattes, “Paul Sabatier, prix Nobel de chimie 1912: un universitaire régionaliste et chercheur de talent,” *l’actualité chimique*, **2012**, *No. 367-368*, 8-18. Lattes writes that Sabatier ended a 1901 lecture before the Toulouse section of the Société Chimique de France in which his newly-found catalytic hydrogenation route was contrasted with Berthelot’s HI-method, with the phrase: “Plus de tube scellé, plus d’œil crevé!” (“No more sealed tubes, no more ruptured eyes!”) pp. 13-14.
5. B. Weckhuysen, Plenary Lecture, CHAINS 2018, Veldhoven, The Netherlands. One of us attended this lecture

- (RvV), and this effectively was the catalyst for the present paper.
6. P. Sabatier and J.-B. Senderens, "Hydrogénations directes réalisées en présence du nickel réduit: préparation de l'hexahydrobenzène," *C. R. Acad. Sci. Paris*, **1901**, 132, 210-212.
 7. It does, however, contain the first description of what would later be called the "Sabatier principle:" cf. M. Boudart, "Correlations in Heterogeneous Catalysis," *Chem. Eng. Progress*, **August 1961**, 57, 33-41. Unfortunately it leaves out any mention of previous formulations of the pertinent idea, due to Mercer, Playfair and Deacon: see A. Mittasch, "Über die Entwicklung der Theorie der Katalyse im neunzehnten Jahrhundert," *Die Naturwissenschaften*, **1933**, 21, 729-732, 745-749 on 745, or, more fully, A. Mittasch and E. Theis, *Von Davy und Döbereiner bis Deacon, ein halbes Jahrhundert Grenzflächenkatalyse*, Verlag Chemie, Berlin, 1932, pp 126-129.
 8. P. Sabatier and J.-B. Senderens, "Hydrogénation de divers carbures aromatiques," *C. R. Acad. Sci. Paris*, **1901**, 132, 1254-1257.
 9. P. Sabatier, *La catalyse en chimie organique*, C. Béranger, Paris, 2nd ed., 1920 (first published 1913), translated by E. Emmet Reid as *Catalysis in Organic Chemistry* (1922), in P. H. Emmett, Ed., *Catalysis, Then and Now*, Franklin Pub. Co., Englewood, NJ, 1965, Part II.
 10. N. Kijner, "Ueber die Constitution von Hexahydrobenzol," *J. prakt. Chem. [2]*, **1897**, 56, 364-372.
 11. Aspects of the story also feature in E.W. Warnsdorff, "The Curiously Intertwined Histories of Benzene and Cyclohexane," *J. Chem. Educ.*, **1996**, 73, 494-497, where more of the 19th-century structural theory context is provided.
 12. All of the parts are M. Berthelot, "Méthode universelle pour réduire et saturer d'hydrogène les composés organiques," *Bull. Soc. Chim. Paris, nouv. sér.* The individual parts are: —, **1868**, 9, 8-31; —, "2^e partie – Suite," **1868**, 9, 91-103; —, "III^e partie – Corps azotés," **1868**, 9, 178-191; —, "Suite – IV^e partie – carbures complexes et polymères," **1868**, 9, 265-300; —, "Suite – IV^e partie – carbures complexes et polymères," **1869**, 11, 4-35; —, "Suite – IV^e partie – carbures complexes (suite et fin)," **1869**, 11, 98-118; —, "Suite et fin – 5^e et dernière partie – matières charbonneuses," **1869**, 11, 278-286.
 13. Ref. 12, **1868**, 9, pp 16-29.
 14. Cf. Hans Meyer, *Analyse und Konstitutions Ermittlung Organischer Verbindungen*, 3rd ed., Springer Verlag, 1916 (digitized version 2013).
 15. A. Baeyer, "Ueber die Reduction aromatischer Kohlenwasserstoffe," *Ber. Dtsch. Chem. Ges.*, **1867**, 1, 127-129.
 16. M. Berthelot, "Remarques sur la méthode universelle pour réduire et saturer d'hydrogène les composés organiques," *Bull. Soc. Chim. Paris, nouv. sér.*, **1868**, 10, 435-439.
 17. Ref. 12, **1869**, 11, p 4.
 18. A. Baeyer, "Ueber die Reduction aromatischer Kohlenwasserstoffe durch Jodphosphonium," *Liebigs Annalen*, **1870**, 155, 266-281.
 19. M. Berthelot, "Sur la transformation des carbures aromatiques en carbures forméniques," *Bull. Soc. Chim. Paris*, **1876**, 26, 146-149.
 20. F. Wreden, "Ueber die Hydrogenisation des Benzols und seiner Homologen," *Liebigs Annalen*, **1877**, 187, 153-167.
 21. C. Graebe, "Ueber die s.g. Additionsproducte der aromatischen Verbindungen," *Liebigs Annalen*, **1868**, 146, 66-73.
 22. A. Horstmann, "Ueber die physikalischen Eigenschaften des Benzols," *Ber. Dtsch. Chem. Ges.*, **1888**, 21, 2211-2222.
 23. M. Berthelot, "Sur l'hydrogénation de la benzine et des composés aromatiques," *C. R. Acad. Sci. Paris*, **1877**, 85, 831-836.
 24. M. Berthelot, "Les polymères de l'acétylène – Synthèse de la benzine," *Bull. Soc. Chim. Paris, nouv. sér.*, **1867**, 7, 303-310. M. Berthelot, "Action de la chaleur sur quelques carbures d'hydrogène," *Bull. Soc. Chim. Paris, nouv. sér.*, **1866**, 6, 268-281. It is essentially a condensation reaction of pure acetylene at elevated temperatures. Benzene is by no means the only product, but apparently the major one.
 25. Cf. Ursula Klein, *Experiments, Models, Paper Tools. Cultures of Organic Chemistry in the Nineteenth Century*, Stanford University Press, 2003.
 26. A. Baeyer, "Ueber die Constitution des Benzols [Neunte Abhandlung]," *Liebigs Annalen*, **1894**, 278, 88-116.
 27. N. Kishner, "Hydrirung des Benzols," *Ber. Dtsch. Chem. Ges.*, **1891**, 24, 559. N. Kishner, "Ueber die Hydrirung von Benzol," *Ber. Dtsch. Chem. Ges.*, **1893**, 26 Bd. IV, 96.
 28. H. Decker, "Wladimir Wasiliewitsch Markownikow" [Obituary], *Ber. Dtsch. Chem. Ges.*, **1905**, 38, 4249-4262.
 29. Cf. W. Markownikoff, "Ueber die Heptanaphtensäure (Hexahydrobenzoësäure)," *Ber. Dtsch. Chem. Ges.*, **1892**, 25, 3355-3366.
 30. O. Aschan, "Ueber die in den Erdölen aus Baku vorkommenden Säuren mit niedrigerem Kohlenstoffgehalt," *Ber. Dtsch. Chem. Ges.*, **1892**, 25, 3661-3670.
 31. O. Aschan, "Ueber das Vorkommen von Methylpentamethylen in kaukasischem Petroleumether," *Ber. Dtsch. Chem. Ges.*, **1898**, 31, 1803-1806. O. Aschan, "Ueber die Bildung der Adipinsäure aus der um 80° siedenden Naphtenfraction des russischen Petroleumäthers," *Ber. Dtsch. Chem. Ges.*, **1899**, 32, 1769-1772. And cf. also O. Aschan, "Zur Genese der Naphtene und der Naphtensäuren," *Liebigs Annalen*, **1902**, 324, 1-39.

32. Kijner, Ref. 10. W. Markownikoff, "Bemerkungen zu Zelinsky's 'Untersuchungen in der Hexamethylenreihe,'" *Ber. Dtsch. Chem. Ges.*, **1897**, *30*, 1211-1214. Unfortunately, for them especially, S. F. Birch in his Obituary Notice "Nicholas Dimitrivich Zelinsky," *J. Chem. Soc. (Resumed)*, **1954**, 4062-4064, writes that Zelinsky was the first to observe a change in ring size, in the cyclo-pentane/cyclo-hexane system, in 1905, citing a reaction involving $\text{AlBr}_3/\text{Br}_2$, where essentially the same observation had already been made by Kijner and Markovnikov in 1891-1898: see W. Markownikoff, "Derivate der Naphten- oder Cyclohexanreihe," *Liebigs Annalen*, **1898**, *302*, 1-42.
33. W. Markownikoff, "Derivate," Ref. 32. O. Aschan, "Ueber die Bildung," Ref. 31.
34. W. Markownikoff and M. Konovalow, "Untersuchungen über die Isomeren des Hexanaphtens (Cyclohexan)," *Ber. Dtsch. Chem. Ges.*, **1895**, *28*, 1234-1237. Konovalov's method was applicable to cyclic paraffins containing a tertiary hydrogen, e.g., MCP. This hydrogen atom was replaced with a nitro-group, which could then be reduced to an amine moiety employing tin and hydrochloric acid. (More on this in Ref. &&42.)
35. W. Markownikoff, "Ueber Methylcyclopentane verschiedenen Ursprungs und einige ihrer Derivate," *Ber. Dtsch. Chem. Ges.*, **1897**, *30*, 1222-1226.
36. W. Markownikoff, "Ueber die Einwirkung von Jodwasserstoffsäure auf einige cyclische Verbindungen bei hoher Temperatur," *Ber. Dtsch. Chem. Ges.*, **1897**, *30*, 1214-1221. cf. A. Hantzsch, "Umwandlung von Derivaten von Pentamethylen in solche des Benzols, Pyridins und Thiophens," *Ber. Dtsch. Chem. Ges.*, **1889**, *22*, 2827-2853.
37. W. Markownikoff, "Derivate," Ref. 32, on pp 36-37.
38. G. A. Olah, A. Molnár, G. K. Surya Prakash, *Hydrocarbon Chemistry*, 3rd ed., John Wiley & Sons, 2017, p 240.
39. C. D. Nenitzescu and I. P. Cantuniari, "Durch Aluminiumchlorid katalysierte Reaktionen, VI. Mitteil.: Die Umlagerung des Cyclohexans in Methyl-cyclopentan," *Ber. Dtsch. Chem. Ges.*, **1933**, *66*, 1097-1100.
40. N. D. Zelinsky and E. M. Tarassowa, "Verhalten der Cycloparaffine bei der Friedel-Craftsschen Reaktion (eine Richtigstellung)," *Ber. Dtsch. Chem. Ges.*, **1932**, *65*, 1249-1252. C. D. Nenitzescu and J. Chicos, "Durch Aluminiumchlorid katalysierte Reaktionen, V. Mitteil.: Über die bei der Kondensation von Cyclohexan und Acetylchlorid entstehenden Verbindungen," *Ber. Dtsch. Chem. Ges.*, **1933**, *66*, 969-971. C. D. Nenitzescu and C. N. Ionescu, "Durch Metall-halogenide katalysierte Reaktionen. I. Über die Einwirkung von Aluminiumchlorid auf Halogenverbindungen in Gegenwart von Cycloparaffinen," *Liebigs Annalen*, **1931**, *491*, 189-210, on p 197.
41. Cf. E. Knoevenagel, "Über die katalytischen Wirkungen des Jods," *J. prakt. Chem. (2)*, **1914**, *89*, 1-50.
42. W. Markownikoff, "Aus dem Gebiete der cyklischen Verbindungen," *Liebigs Annalen*, **1899**, *307*, 335-367, on p. 335.
43. H. A. Smith, "The Catalytic Hydrogenation of Aromatic Compounds," in P. H. Emmett, Ed., *Catalysis*, Reinhold Publ. Corp., 1957, Vol. 5, Ch 4.
44. Note also that *both* Berthelot's 1869 work on the H₂-hydrogenation of coal (Ref. 12, last item) *and* Sabatier's early 1900s work on catalytic hydrogenation were important inspirations for the early German efforts to develop a coal-to-oil conversion process, 1910-1925. See, e.g., F. Fischer, "Neue Möglichkeiten der Ölgewinnung aus Kohle," *Abh. Kohle*, **1920**, *4*, 458-470 and "Chemie und Kohle," *Brennstoff-Chemie*, **1927**, *14*, 226-231.

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