

# Pioneering Ideas for the Physical and Chemical Sciences

Josef Loschmidt's Contributions and  
Modern Developments in Structural  
Organic Chemistry, Atomistics,  
and Statistical Mechanics

Proceedings of the Josef Loschmidt Symposium,  
held June 25 – 27, 1995, in Vienna, Austria

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# LOSCHMIDT'S GRAPHIC FORMULAE OF 1861

## Forerunners of Modern Structural Formulae

Alfred Bader

Milwaukee, Wisconsin

I first became aware of the work of Josef Loschmidt through a letter (Fig. 1) that my old friend, William Wiswesser, sent to Linus Pauling in 1987. He described in a wonderfully clear manner what Loschmidt had published in 1861 in a privately printed book, *Chemische Studien*<sup>1</sup>. Bill sent me a copy of this letter and included Loschmidt's fold-out plates, which Bill had hand-colored.

Fascinated by Loschmidt's work and hoping that Aldrich could help make chemists aware of this almost unknown man, Bill sent me a manuscript for an article which he hoped we would publish in the *Aldrichimica Acta*. His own great contribution to chemistry was the Wiswesser Line Notation, the WLN, which made possible the single-line depiction of every molecule, no matter how complicated. At a time when computers were in their infancy, this was so useful that Aldrich offered its catalog in WLN. Unfortunately, Bill's paper dealt mainly with Loschmidt's structures as forerunners to the WLN, and I found it too narrowly focused. However, he was persistent and very much wanted his paper published in the *Acta*, which went to over 200,000 scientists worldwide. My wife, Isabel and I worked with him to broaden his manuscript, and we also enlisted the help of a very able chemist in Vienna, Christian R. Noe, to check on Loschmidt's work and life. Finally, Bill's paper was published<sup>2</sup>, and I remember his delight when I sent him the first copies of the *Acta* by express mail. Sadly, he died of a massive heart attack a few days later.

Bill's persistence certainly resulted in my becoming increasingly interested in the remarkable work of this chemist from Bohemia who spent most of his working life in Vienna. In 1861, while still a high school teacher, Loschmidt paid for the publication of a 54-page octavo book, *Chemische Studien*, containing two essays. The main purpose of his work was "to provide a better understanding of the constitution of matter."<sup>3</sup> The first essay, of 47 pages, dealt with the shape of molecules and was entitled "*Constitutions-Formeln der organischen Chemie in (geo)graphischer Darstellung.*" The copy of the book in the National Library in Vienna bears the title '...geographischer...'; all the other copies examined bear the title '...graphischer...'. Presumably the version in Vienna is a galley proof, which he changed from 'geographischer' to 'graphischer.' Fig. 2, showing the headings of the chapters, indicates how clearly and logically the essay was constructed.

3124 Stuidts Ferry Road  
Reading, PA 19605  
'87 August 2

Dr. Linus Pauling  
440 Page Mill Road  
Palo Alto, CA 94306

Dear Linus:

Every paragraph of your June 23rd reply was a therapeutic delight while I was feebly recovering from a near-fatal coronary blood clot. I'm thankful that my daughter— living next door-- got me to the hospital in time: half a pumping heart is far better than none!

Now you should be delighted to see on an enclosure that your "bent bond" is the cover story of the July JOURNAL OF CHEMICAL EDUCATION just received: Claude Wintner's reference 5 acknowledges that you introduced this "tau bond" in 1960. As you stated in your Hawaiian festival lecture some years ago, your bent bond is superior to MO alternatives in predicting shorter double and still shorter triple bond lengths. But I'll bet very few in that large overflow audience knew that Josef Loschmidt had pictured just such shortenings in his 1861 masterwork diagrams! First appreciate the "state of the art" in 1861, as this same July J. CHEM. ED. verified it on page 574:

"In van't Hoff's lifetime, chemistry and the way chemists thought about matter and reactions changed dramatically, and he must be regarded as one of the prime movers in bringing about these changes. ((With Boltzmann, a beer-drinking friend of Loschmidt!)) He told the story of how, when he went to school in Rotterdam, the lower forms were taught that the formula of water was HO, but word filtered down from the upper forms that a different formula, H<sub>2</sub>O, might be gaining acceptance. So much for the state of the art in the early 1860's." (I have a few oldies of the 1870's with "HO" for water.)

Now note Loschmidt's amazingly perceptive graphical visualizations of 1861: CH<sub>3</sub>CH<sub>3</sub> in fig.9 vs overlapping CH<sub>2</sub>:CH<sub>2</sub> in 56 & 57, vs still tighter CHCH (as it was printed in the 1860's) and triple-bond marks in fig.59. Other "vinyloid" CH:CH bonds are pictured in figs. 58, 65-71, 73, 75, 82, 86, 113, 115, 143, 144, 213, 219-222 (all highlighted as double-blue sets), and I probably missed some.

O-atoms with overlapping double bonds are dominated by Loschmidt's carbonyl examples, almost too numerous to recite and highlight in "sulfur yellow": figs. 4, 5, 7, 8, 12-17, 20-22, 25-26, 29, 32, 33, 36, 41-55, and so on, with N-atoms in figs. 177, 179a, 180; and with S-atoms in most of the S-compounds from fig. 320 (OSO) to the last fig.368. Very few are missing the tiny double-bond mark.

N-atoms with overlapping double-bond marks begin at fig. 95 and dominate Plate 3 with a triazine CYCLIC series (figs. 151-158, etc.), there showing ONN as a cyclic fig. 176. (Note analogous figs. 68, 86, and 319 with valid 3-atom rings; figs. 268-9 are dibenzoTRicyclics!)

N-atoms with cyano- or nitrile triple bonds also are bountifully illustrated in Loschmidt's 1861 spectaculars, hardly marred by erroneous links to C<sub>6</sub>H<sub>2</sub>-X rings. All are highlighted with the "greening" of that vital element.

S-atoms with double bonds (to C, N, or O) begin with fig.309 (SCS) and fill most of the remaining diagrams (to 368, many with that bold benzene ring).

Figure 1. Wiswesser's letter to Pauling.

He illustrated this first aspect of the understanding of matter on seven foldout plates, where he depicted 368 structures. These do not, however, deal with 368 compounds, because many were hypothetical, sometimes several structures dealing with just one compound.

His second essay, six pages on gas laws, was a step towards his calculation, four years later, of the Loschmidt Number, the size of molecules. In 1811, Avogadro had predicted that someday someone would be able to make the calculation. In 1865, Loschmidt did so.

## CHEMISCHE STUDIEN

von  
J. Loschmidt

### A. Constitutions-Formeln der organischen Chemie in geographischer Darstellung

Pollenz  
Isomerie  
Kern  $C_2^v$ . Aethyl - Reihe  
Kern  $C_2^{iii}$ . Vinyl - Reihe  
Kern  $C_3^{vii}$ . Propyl - Reihe  
Kern  $C_3^v$ . Propylen and Allyl - Reihe  
Zucker  
Mehrbasische Säuren  
Stickstoff  
Amidverbindungen  
Imidverbindungen  
Stickstoffoxyde  
Kern  $C_6^v$ . Phenyl - Reihe  
Kern  $C_7^{viii}$ . Benzyl - Reihe  
Anilin  
Phenylharnstoff  
Harnsäure  
Schwefel

### B. Das Mariotte'sche Gesetz

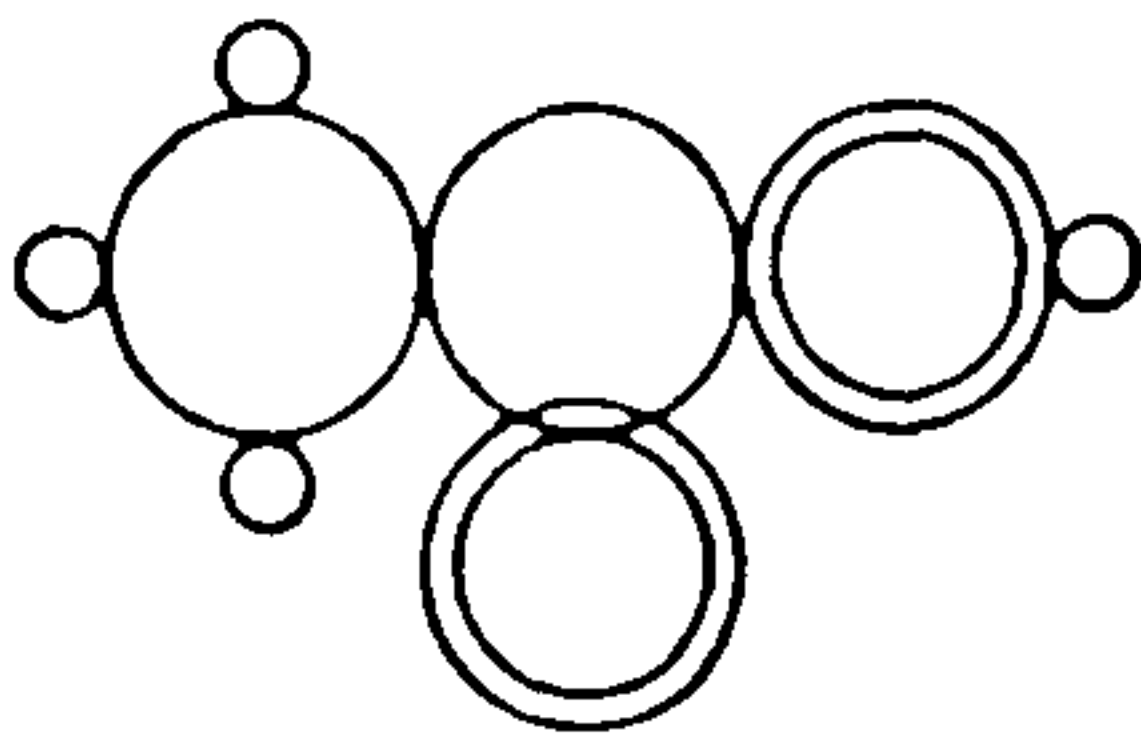
Spannkraft der Gase

Figure 2. Chapter headings in *Chemische Studien*.

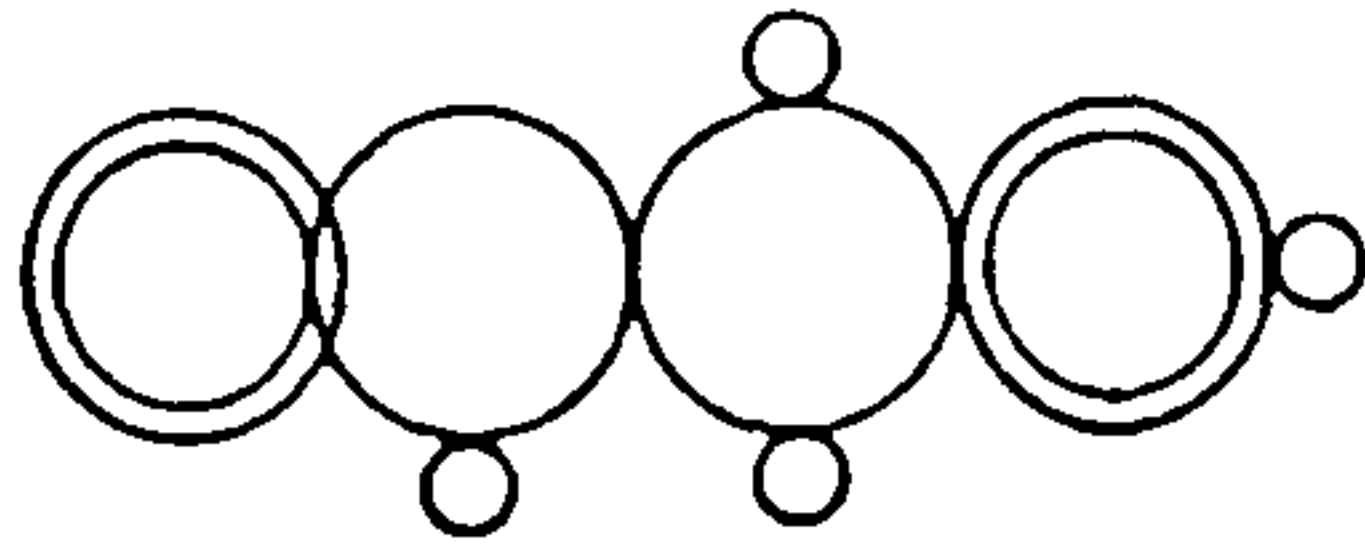
A simple example of how Loschmidt arrived at his structures is that of acetic acid (Fig. 3). He presented four alternatives — 21, 22, 23a, and 23b — and then, through consideration of the reaction of acetic acid with alkali and its relation to formic acid, determined that 21 was correct. His method was to present various hypotheses and eliminate those he considered impossible or unlikely. Understandably, he was not always correct. With urea, for instance, he showed two possible structures — his Schemata 168 and 169 — but chose the wrong one (Fig. 4).

These molecular formulae, which are easily understood by us today, were so strange to his contemporaries that they ignored his work. It was not until 1912 that Richard Anschütz, the first chemist to study Loschmidt's book critically and objectively, pointed out how very much better Loschmidt's structures were than those of any of his contemporaries, Kekulé included. Anschütz had such great difficulty finding *Chemische Studien* and believed it was so important that he decided to publish a re-formatted version<sup>4</sup> which was much easier to read because he moved the structures from the fold-out plates to the text. He also included a short biography and many footnotes, which are particularly helpful. In footnote 3 (Fig. 5), for instance, Anschütz illustrated August Kekulé's structure of acetic acid and commented that it was inferior to Loschmidt's.

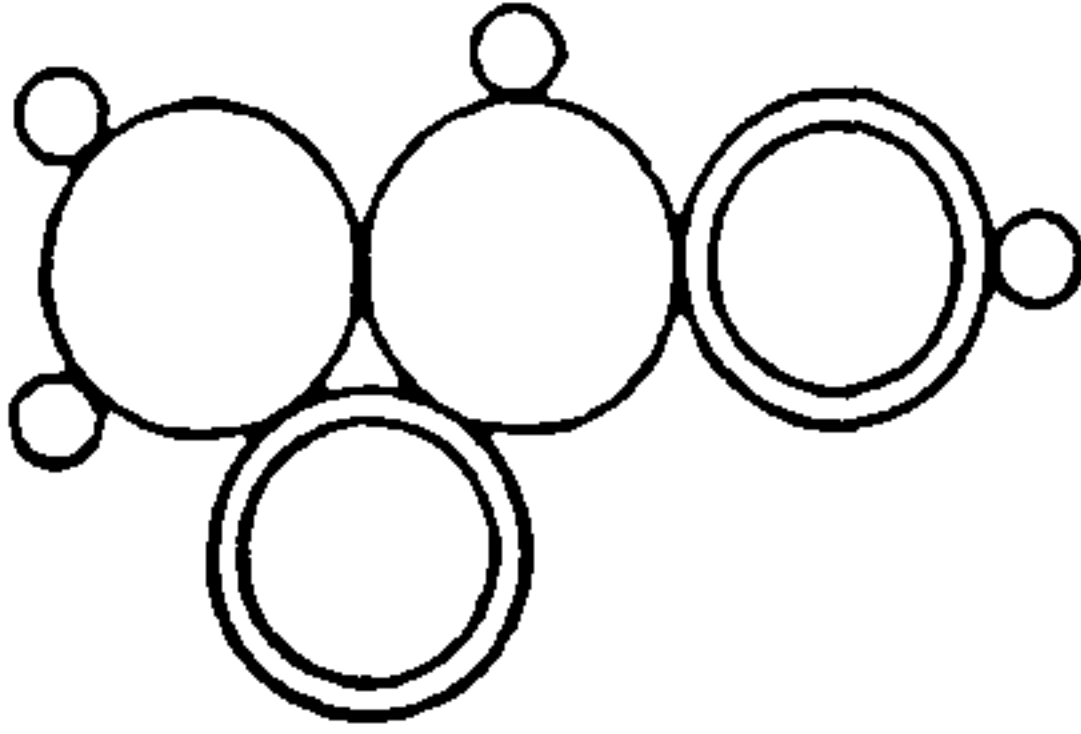
He realized that Loschmidt had been the first to depict many compounds correctly. One of these 'firsts' was the presentation of ozone as  $O_3$ . Another first, perhaps the most



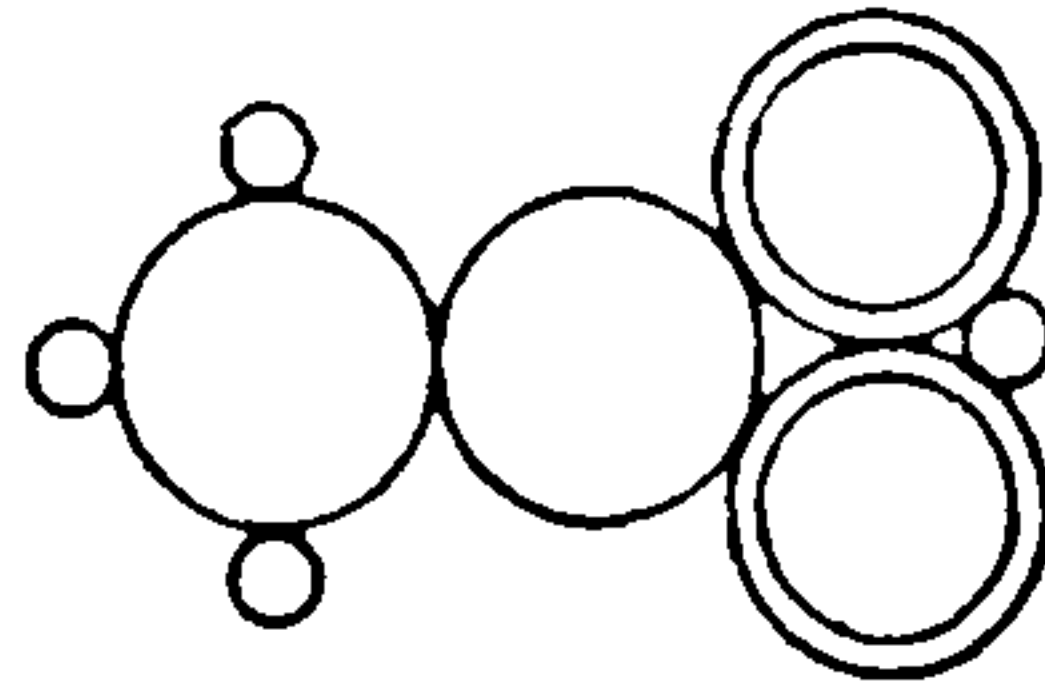
Schema 21



Schema 22

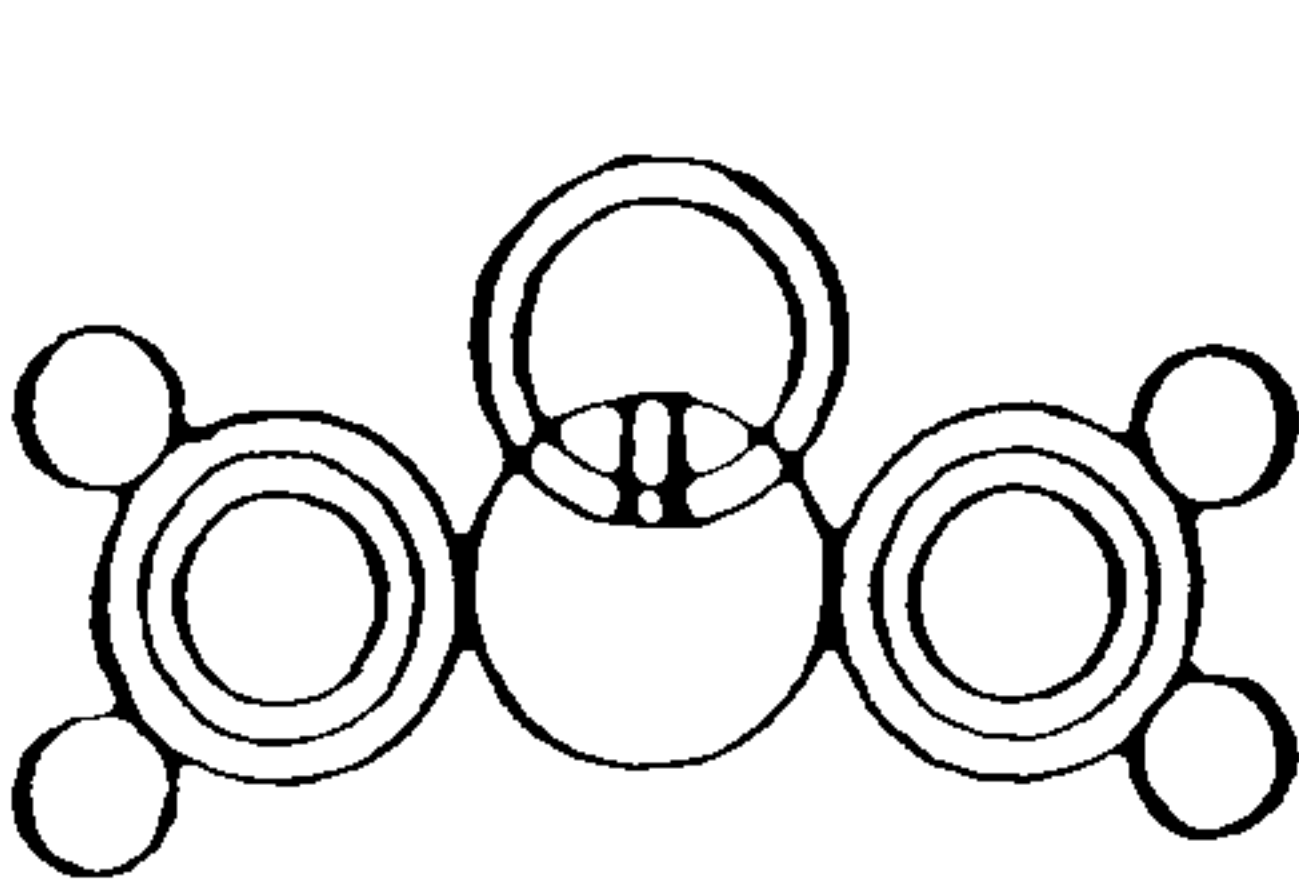


Schema 23a

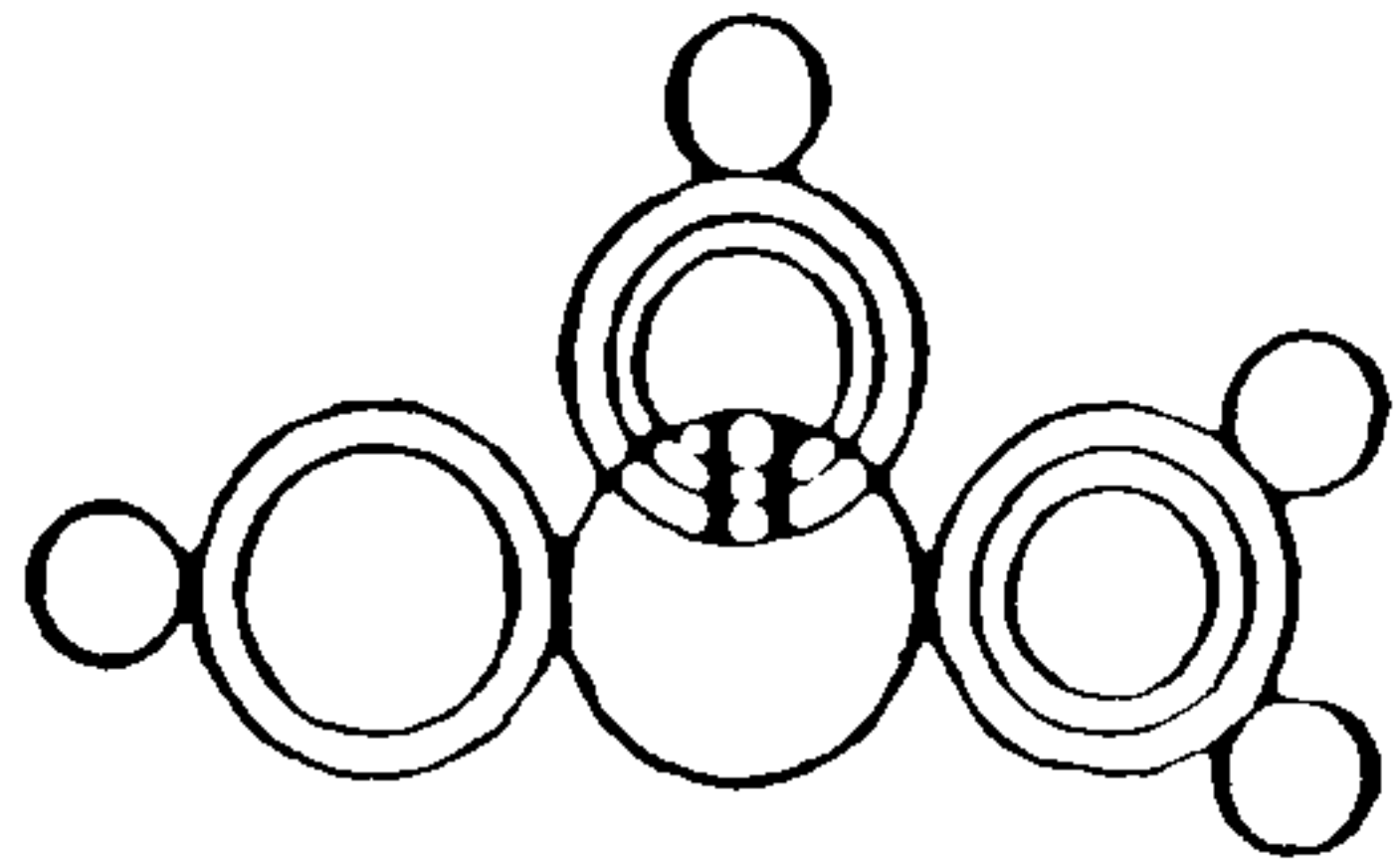


Schema 23b

Figure 3. Acetic acid.



Schema 168



Schema 169

Figure 4. Urea.

3) Zu S. 5. Weder Couper, noch Kekulé hatten die mehrfache Bindung durch Bindungsstriche zum Ausdruck gebracht. Kekulé's graphische Formeln dagegen zeigen die mehrfache Bindung durch die mehrfache Berührung der für die polyvalenten Atome von ihm eingeführten Figuren an. Ich setze Kekulé's graphische Formel der Essigsäure hierher



(Lehrbuch, Bd. 1, S. 165, Anm.). Diese graphische Darstellung ist insofern der Loschmidts unterlegen, als sich auch Figuren von Atomen berühren, die nicht miteinander verbunden gedacht werden. Es sind eben Projektionen von Atommodellen, die in ganz bestimmter Art und Weise ihrer Wertigkeit entsprechend durch Messingstäbe zusammengehalten werden können, die die Modelle durchsetzen.

Figure 5. Kekulé's acetic acid in 1861.

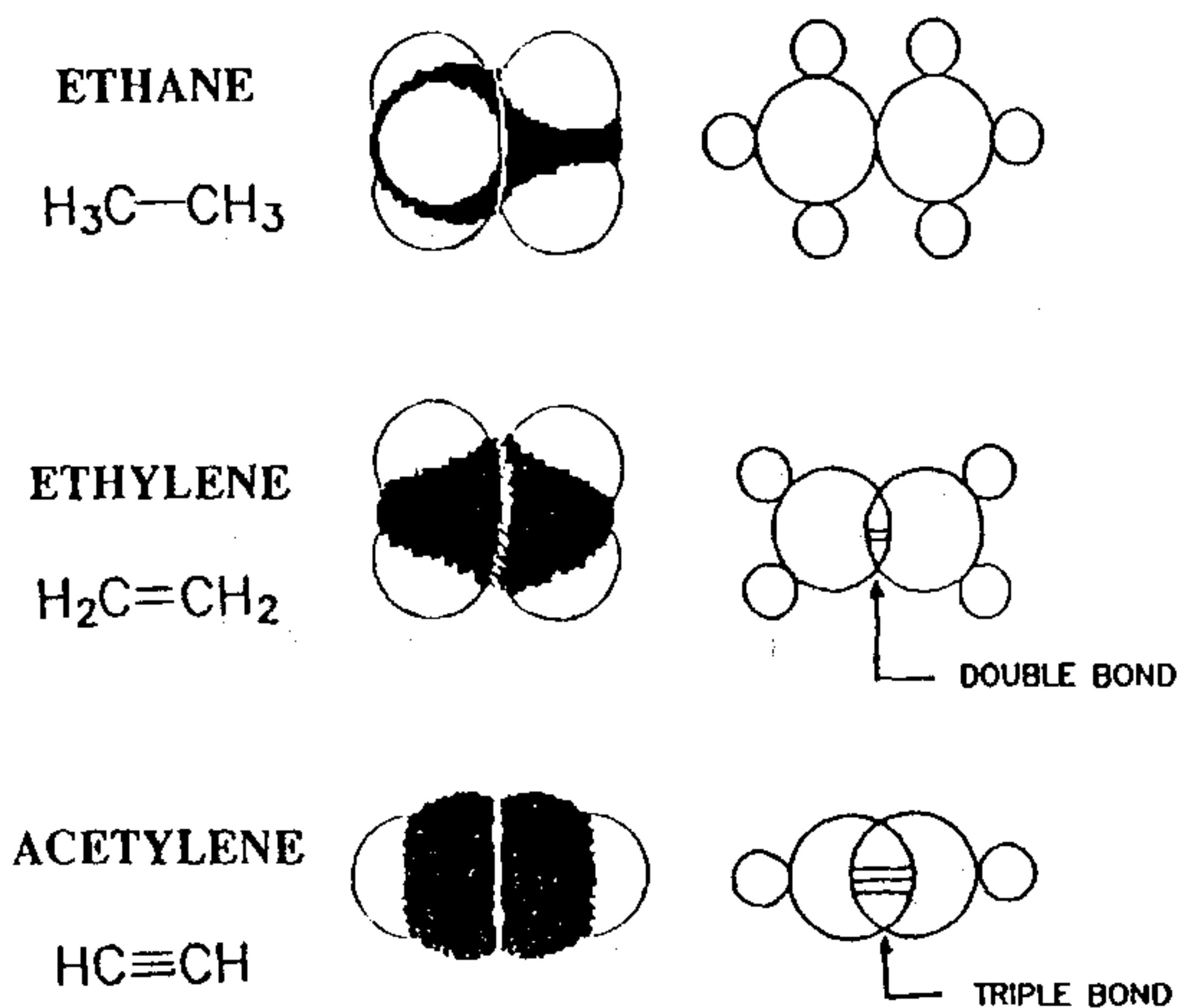


Figure 6. Double and triple bonds.

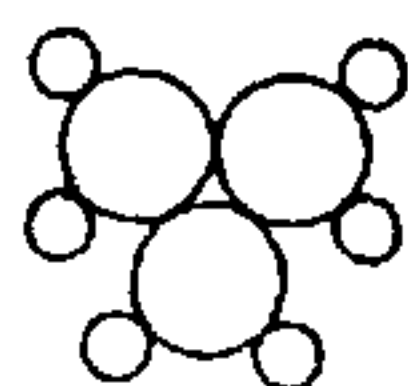
visionary of all, was his depiction of ethylene and acetylene (Fig. 6) with overlapping atoms, stronger with acetylene than ethylene. Here for the first time double and triple bonds were shown as we show them today.

Loschmidt was the first to propose a carbocyclic compound, cyclopropane. In his discussion of propylene,  $C_3H_6$ , he considered the possibility of a cyclic structure, Schema 68 (Fig. 7). Cyclopropane was not made until some twenty years later, but Loschmidt stated that it was a possibility. He pointed out that this question would be solved when it was clear whether two different hydrocarbons —  $C_3H_6$  — existed. Of course, today we know that these are propylene and cyclopropane.

Recently, F.W. Lichtenthaler<sup>5</sup> has shown (Fig. 8) how Adolf Baeyer, Hugo Schiff and Rudolph Fittig depicted sugars around 1870. Loschmidt's structures (Fig. 9) nine years earlier were very much clearer. This was appreciated by Anschütz, but goes uncited by modern

Der zweite

Ansatz, der einer anderen Gestaltung des Kernes, ist im Sch. 68 für  $C_3H_6$  angedeutet<sup>61)</sup>. Diese Verkettung der Kohlenstoffatome hat, im Hinblick auf das gleiche Verhalten anderer mehrstelliger Atome, an sich nichts Unwahrscheinliches; [15] sie drängt sich sogar, wie wir weiter unten beim Phenyl sehen werden, in manchen Fällen als die akzeptabelste Supposition auf. Die Frage wird sich übrigens für diese Kerne entscheiden lassen, wenn man untersuchen wird, ob es zwei verschiedene Kohlenwasserstoffe  $C_3H_6$  gebe, ob z. B. der durch Elektrolyse der Buttersäure und der durch Zersetzung des jodwasserstoffsäuren Allyläthers erhaltene, vollkommen identisch seien.



Schema 68.

Figure 7. Cyclopropane.

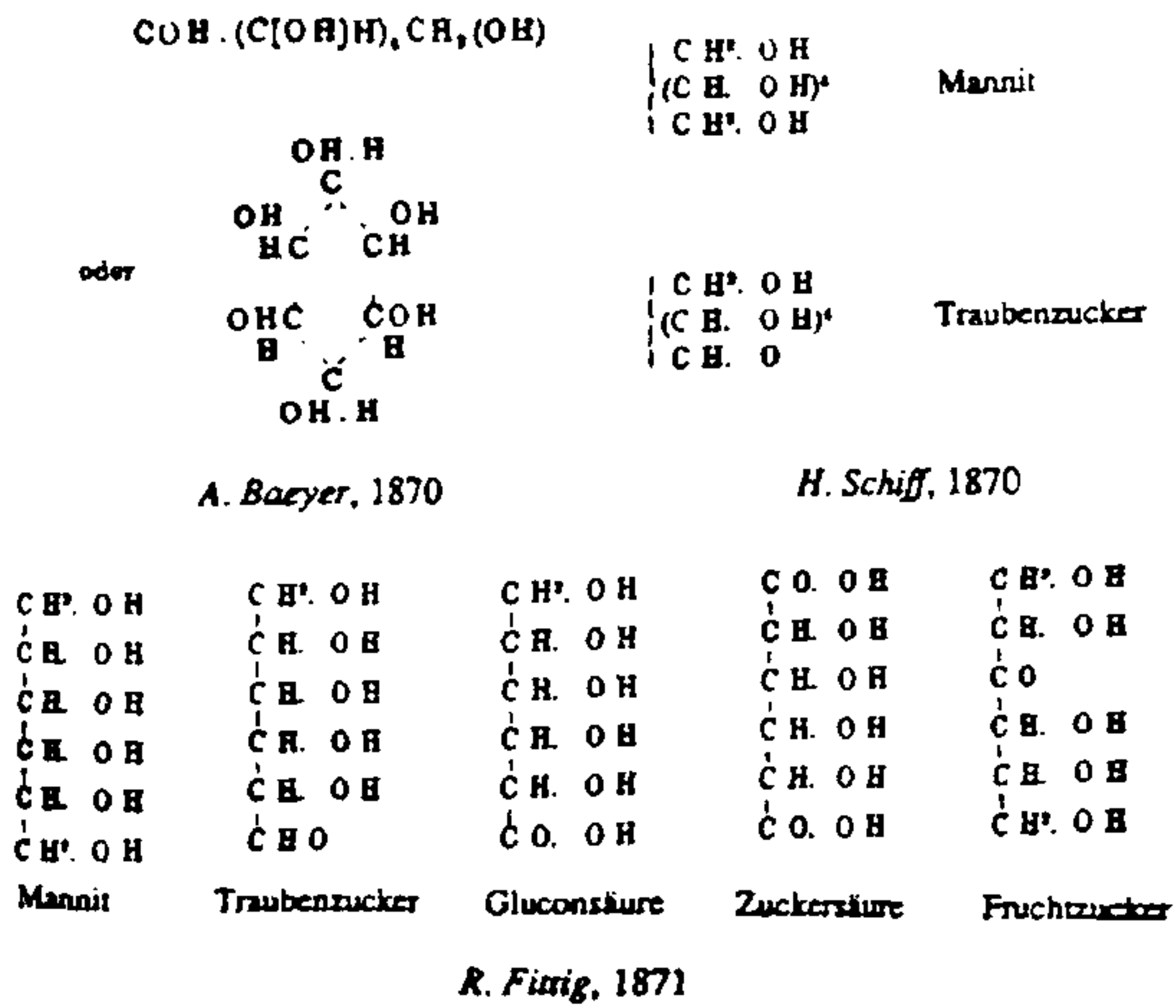


Figure 8. Sugars 1870–71. [From S. W. Lichtenthaler, Emil Fischer's proof of the configuration of sugars: A centennial tribute, *Angew. Chem. Int. Ed.* 31, 1541 (1992).]

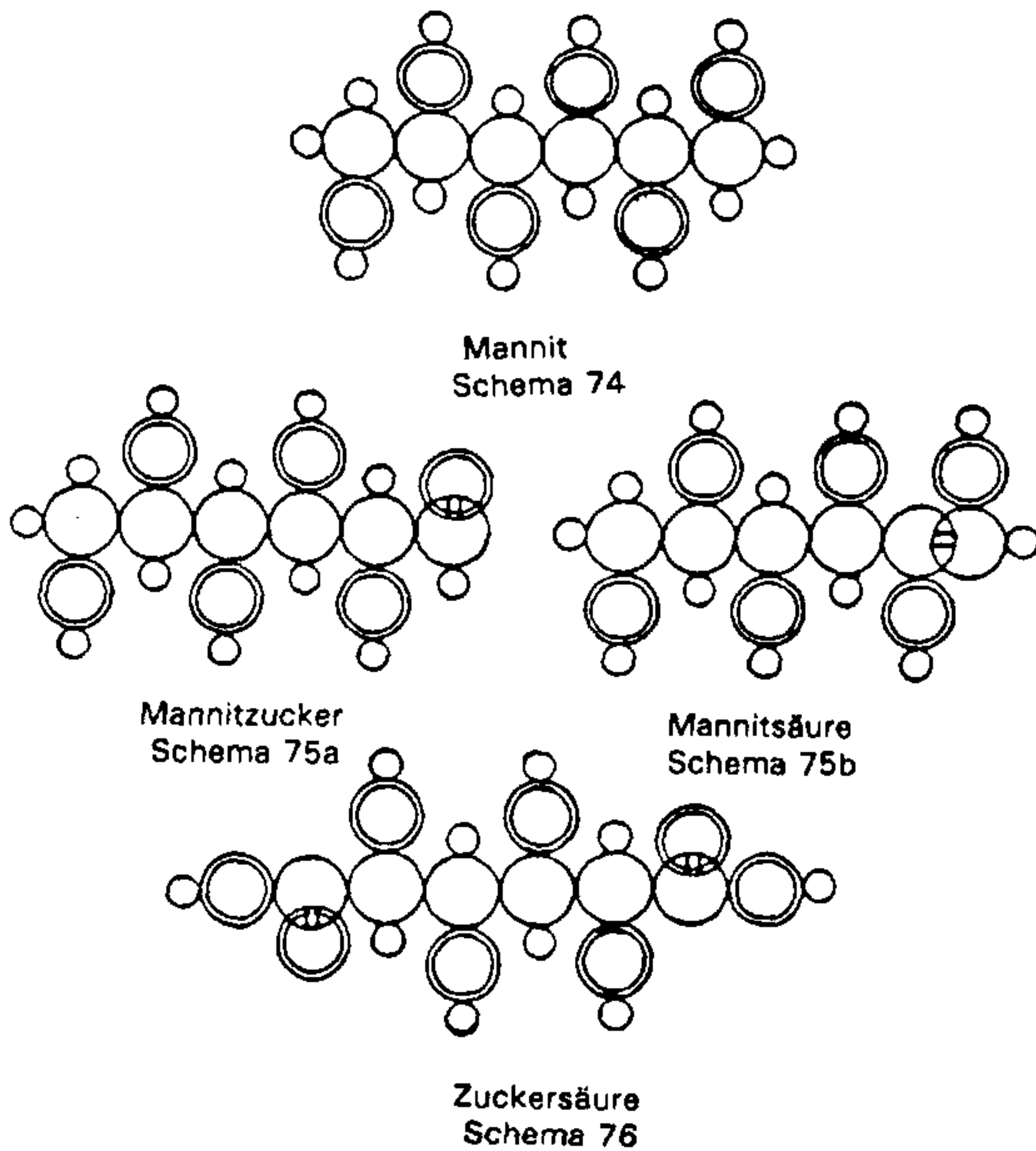


Figure 9. Sugars: Loschmidt, 1861.

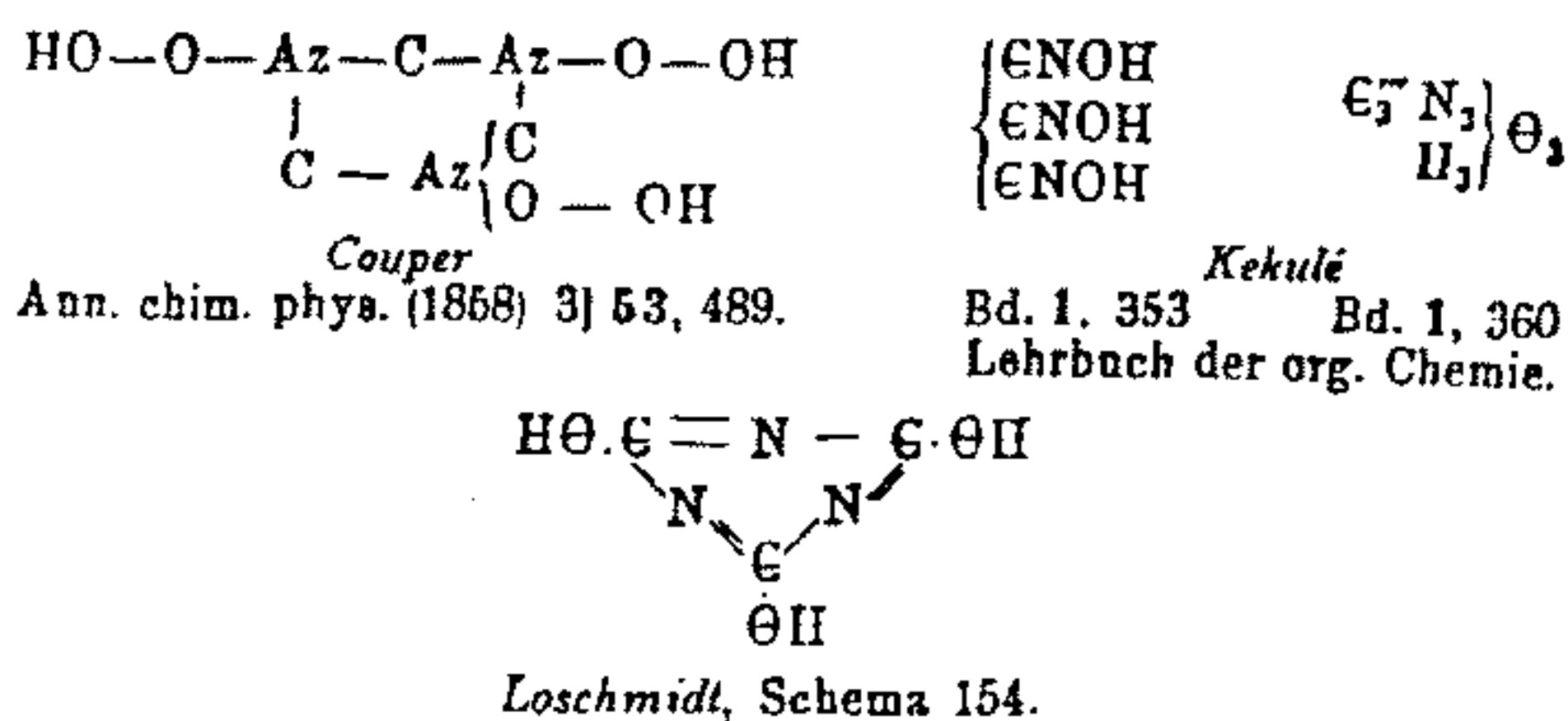


Figure 10. Cyanuric acid.

historians of sugar chemistry. Anschütz pointed out that Loschmidt was the first to show the correct structure of mannitol<sup>6</sup> and the first to consider cane sugar an ether<sup>7</sup>.

He was the first to depict the structure of a heterocyclic correctly. Couper<sup>8</sup> preceded him with cyanuric acid, but, as Anschütz pointed out<sup>9</sup>, Couper's structure was mistaken and Kekulé's not really intelligible, whereas Loschmidt's Schema 154 was clear (Fig. 10).

In his important chapter on isomerism, Loschmidt distinguished clearly between isomers "im engern Sinne" — compounds such as alpha- and beta-toluic acid — and isomers "im weiteren Sinne" — isomers such as nitrotoluene and aminobenzoic acid. He gave another example of isomers in the chapter on polybasic acids (Fig. 11), where he dealt with succinic, malic and tartaric acids and stated that fumaric and maleic acids are isomers "im engern Sinne."

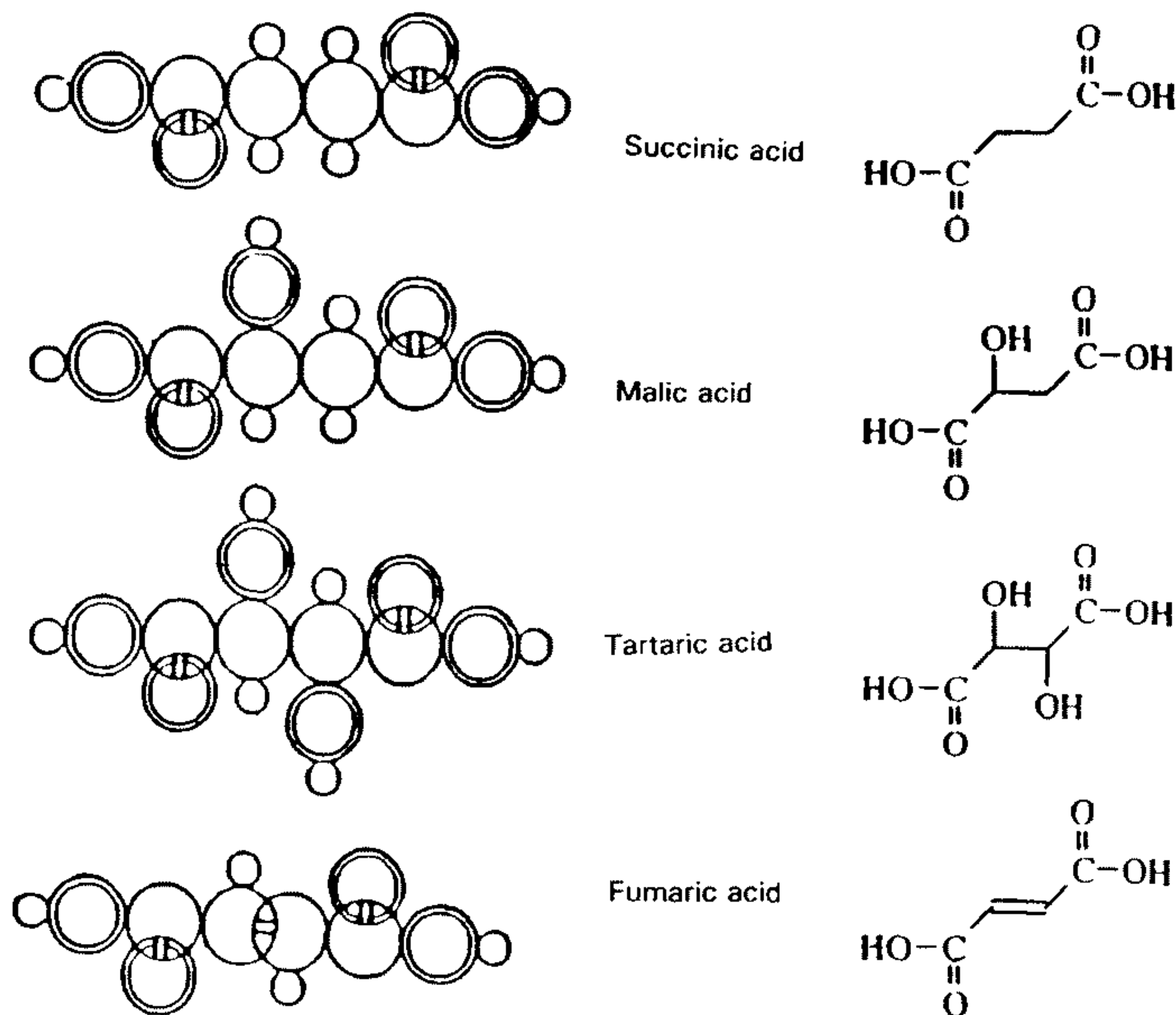


Figure 11. Polybasic acids.

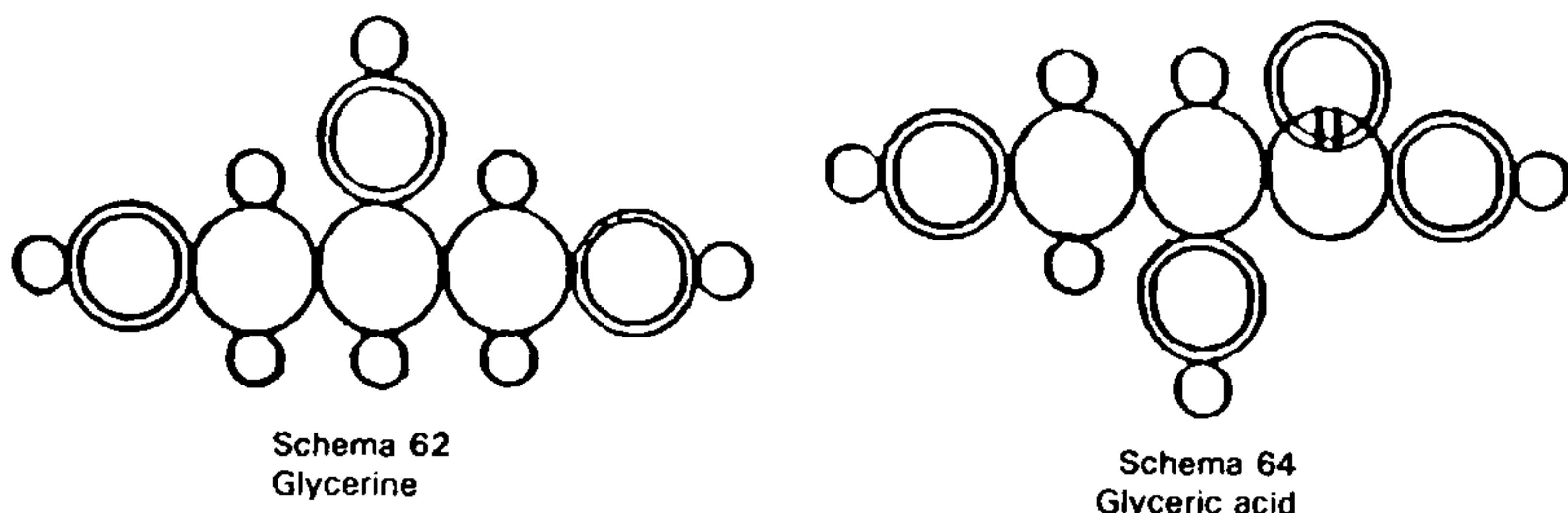


Figure 12. Glycerine and glyceric acid.

When discussing glycerine and glyceric acid (Fig. 12), he stated that with alcohols, there was a rule that each carbon atom could have only one hydroxyl. Anschütz compared<sup>10</sup> (Fig. 13) Couper's and Kekulé's structures of glycerine with Loschmidt's Schema 62, and noted that this was the first version of what we now know as the Erlenmeyer Rule.

While at the time, Kekulé considered sulfur in all compounds to be divalent, Loschmidt considered it to be sometimes divalent, as in carbon disulfide; sometimes tetravalent, as in sulfur dioxide; and sometimes hexavalent, as in dimethyl sulfate (Fig. 14). Anschütz compared<sup>11</sup> three of Loschmidt's structures — his Schemata 344 through 346 (Fig. 15) — with the corresponding structures of Kekulé, pointing out how clear and understandable Loschmidt's structures were. Unfortunately, they were not appreciated by chemists at the time.

In a letter<sup>12</sup> to Emil Erlenmeyer dated January 4, 1862, written just months after the appearance of Loschmidt's *Chemische Studien*, Kekulé characterized Loschmidt's structures as "*Confusionsformeln*." How could Kekulé be so damning? We must understand that most leading chemists at the time did not think it possible to write formulae of constitution. Three years earlier, in 1858, Adolphe Wurtz<sup>13</sup> had faulted Couper for writing such formulae, and Kekulé expressed similar views very clearly in his 1861 textbook<sup>14</sup>:

Which of the different rational formulae one wants to use for specific cases is essentially a question of appropriateness. Based on the observations already given, there can be no doubt that one may use *different rational formulae for the same substance*. At the same time, one

46) Zu S. 25. Die Erkenntnis, daß in mehrstürigen Alkoholen »jedes C nur ein Hd tragen kann«, hat Loschmidt wohl zuerst ausgesprochen. A. S. Couper gibt dem Glycerin noch

die Strukturformel 
$$\begin{array}{c} \text{O} - \text{OH} \\ | \\ \text{C} \left\{ \begin{array}{l} \text{O} - \text{OH} \\ \text{H} \end{array} \right. \quad (\text{O} = 8), \text{ vgl. Ann. chim. phys.} \\ | \\ \text{CH}_2 \\ | \\ \text{C} \left\{ \begin{array}{l} \text{H}_2 \\ \text{O} - \text{OH} \end{array} \right. \end{array}$$

(1858) [3] 53, 487. Kekulé löst in seinem Lehrbuch der organischen Chemie, Bd. II, 124 die auf den verdreifachten Wassertypus bezogene Glycerin-Formel  $\left. \begin{array}{l} \text{C}_3\text{H}_8 \\ \text{H}_3 \end{array} \right\} \Theta_3$  nicht weiter auf.

Figure 13. Glycerine compared.

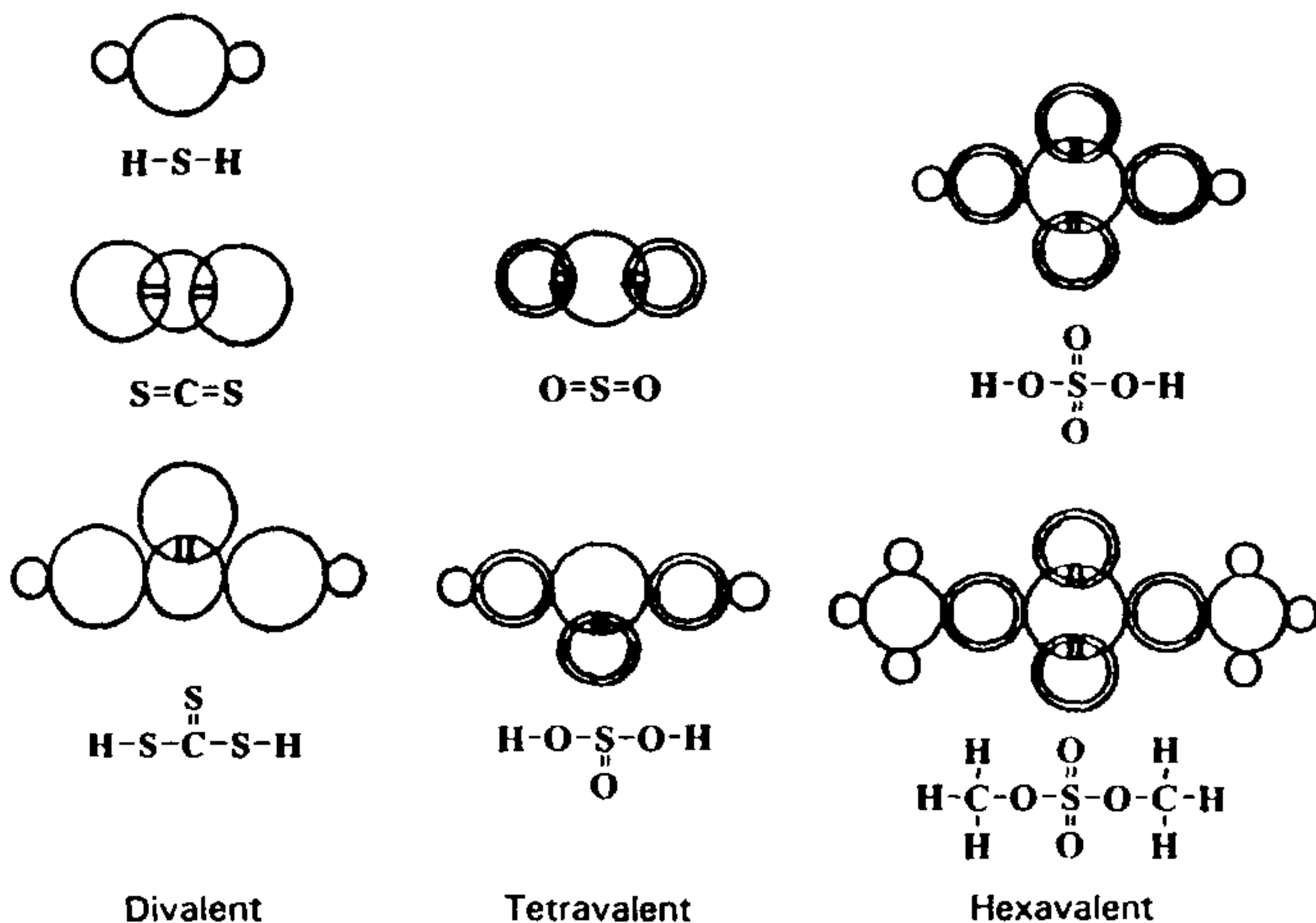


Figure 14. Sulfur.

must also, of course, keep in mind that the rational formulae are only formulae of reactions ('Umsetzungsformeln') and not formulae of constitution ('Constitutionsformeln'), and that they do not in any way describe the constitution, i.e., the position of the atoms in the compounds. ... This should be clearly stressed, because oddly enough some chemists still believe that by the study of chemical reactions, one can derive with certainty the constitution of compounds, and thus depict the positions of the atoms in the chemical formula. That the latter is not possible warrants no special proof... Yet a basic task of natural science must of necessity be to discover the constitution of matter or in other words, the position of atoms; this, however, can only be attained by the comparative study of physical properties of the existing compound and certainly not by the study of chemical reactions... But even when we have succeeded in this, different rational formulae ('Umsetzungsformeln') will still be appropriate. [emphasis supplied]

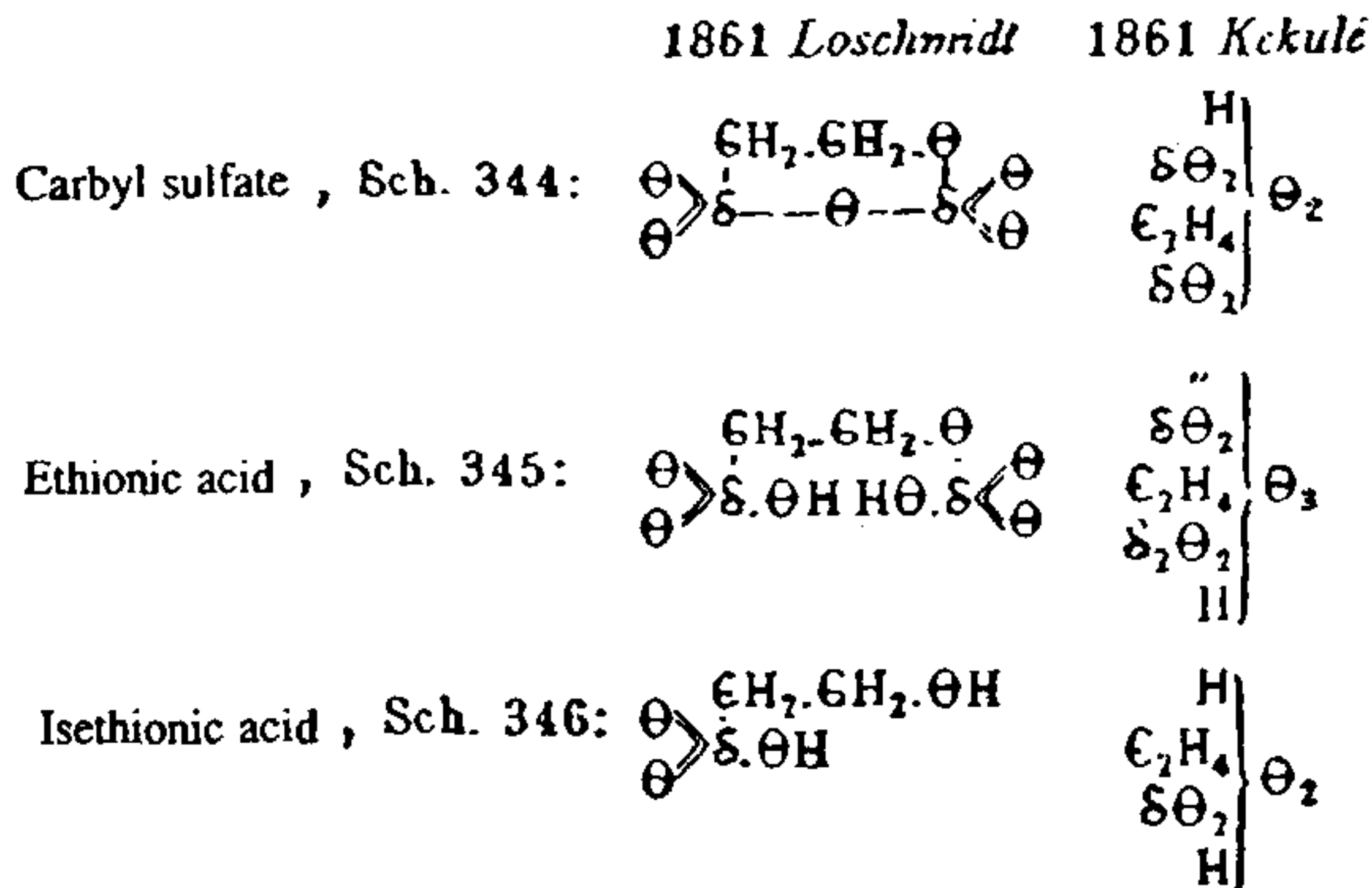


Figure 15. "Ausgezeichnet zutreffend" — Anschütz footnote 193.

Clearly Kekulé believed that it might someday be possible to come to structural formulae, not through a study of reactions, but by comparison of physical properties. Yet in *Chemische Studien*<sup>1</sup>, there were hundreds of such formulae of constitution, proposed by a man about whom no one knew much, if anything. To Kekulé, they were “*Confusionsformeln*”!

His structural formulae, even without aromatics, would suffice to establish Loschmidt as a great chemist. The sections, pages 30–38, dealing with benzene and its derivatives, have resulted in the present controversy as to whether Loschmidt or Kekulé was the first to depict benzene as a six-carbon monocyclic structure.

What did Loschmidt consider the structure of benzene to be? When discussing<sup>15</sup> the possibility of two isomers of  $C_3H_6$ , he postulated the existence of cyclopropane — the first carbocyclic structure suggested — and said “as we will see below with phenyl, such a cyclic structure is in some cases the most acceptable supposition.” Loschmidt again presented several structures — 181, 182, 184 and 185 — for consideration (Fig. 16). Schema 181, the hexatetraene, was easily excluded because, at that time, benzene could not be hydrogenated. Of Schema 182, Loschmidt wrote that here “*könnte man fast versucht sein*”, i.e. one might be tempted to believe this to be the correct structure. To Anschütz, it was clear that Loschmidt had not considered either Schema 181 or 182 satisfactory (“*ihn nicht befriedigenden Schemata 181 und 182*”)<sup>16</sup>. Nonetheless, some historians of science, for instance, A.J. Rocke<sup>17</sup> and G.P. Schiemenz<sup>18</sup> believe that Loschmidt preferred Schema 182 to 185, even though *all* of Loschmidt’s aromatic structures were based on 185. He depicted benzene with unsymmetrically placed hydrogen atoms. At the time, chemists believed that two isomeric salicylic and benzoic acids existed, and so also two benzenes, benzene and parabenzene, tentatively explained by Loschmidt through slightly differently placed hydrogen atoms. Within a few years, the “isomers” were shown to be impure compounds.

Did Loschmidt believe in a 6-carbon monocyclic structure? I believe so, but this has become a “*Glaubensfrage*” — a matter of faith. Schiemenz wrote<sup>19</sup>, “...one must interpret the circular symbol as what it really means and not as what it could be, and hence not as a circular array of six carbon atoms. The argument also holds true for all of Loschmidt’s formulae...which may have some *superficial resemblance* with modern molecular models. *To date molecular modelling back to 1861 is just anachronistic.*” [emphasis supplied] However, I believe the structures are so clear that he should be called ‘the father of molecular modelling’. But as Professor Albert Eschenmoser<sup>20</sup> said after the Symposium in Vienna: “We may never know for certain whether Loschmidt thought of benzene as a monocyclic 6-carbon structure or not.”

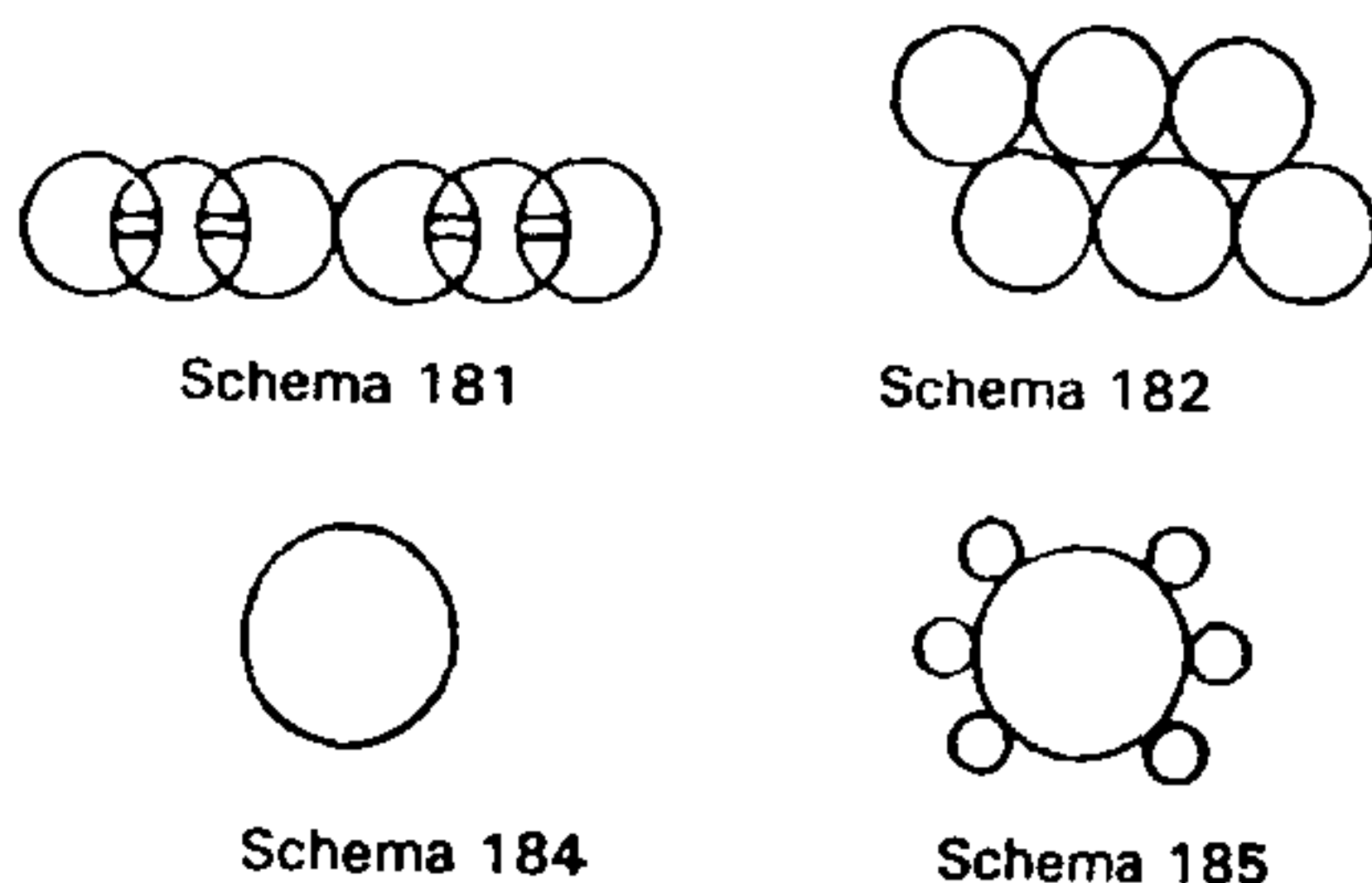


Figure 16. Benzene.

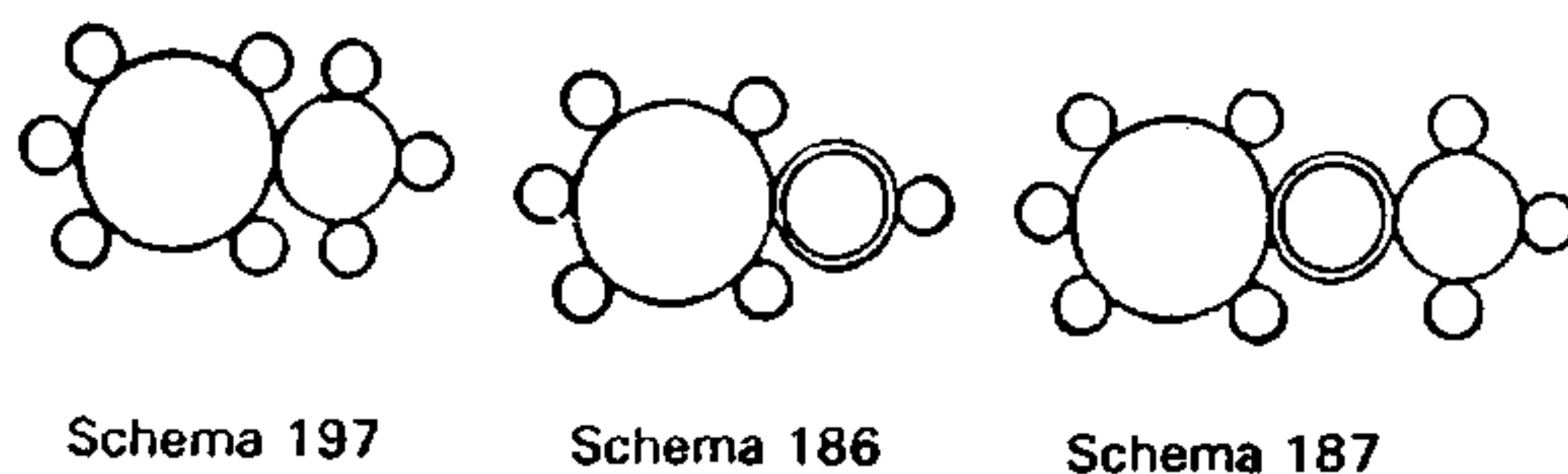
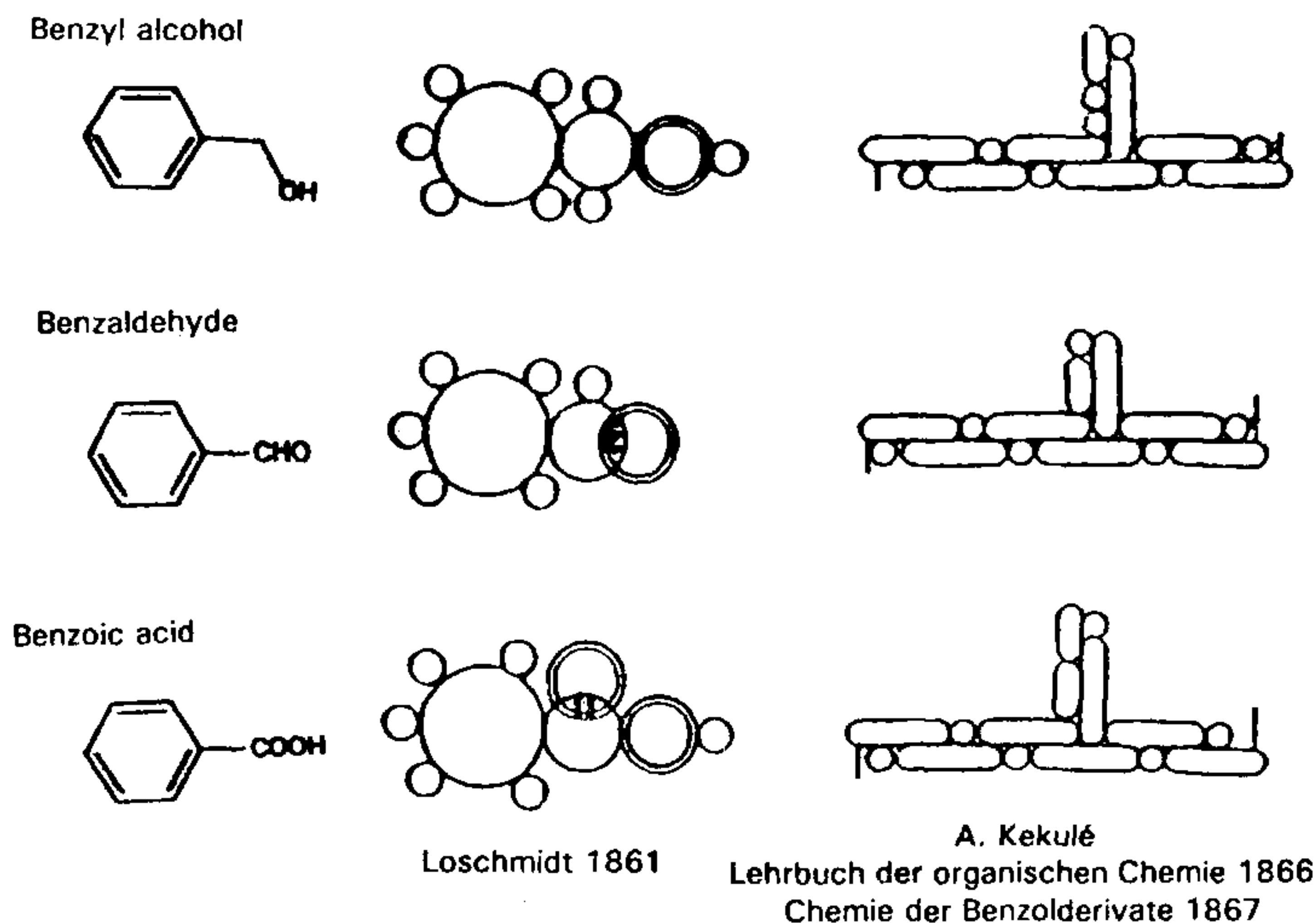


Figure 17. Toluene, phenol, and anisole.

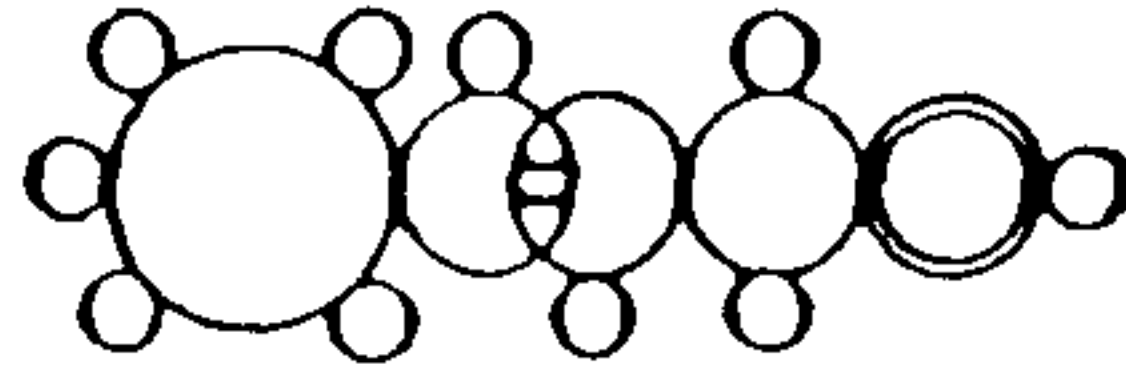
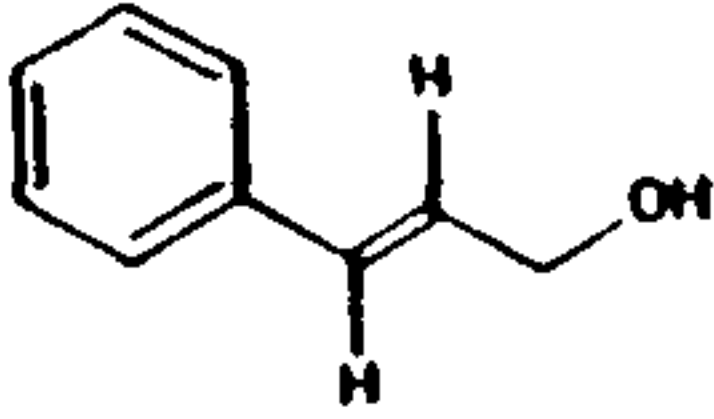
Kekulé's cyclohexatriene structure of 1865 was an improvement over Loschmidt's 185 as Loschmidt did not know how to explain the apparent unsaturation. He wrote<sup>21</sup> "...we can leave our decision *in suspensa*, as our constructions are independent [of the exact structure of benzene]. We take Schema 184 for the nucleus  $C_6^{VI}$  and treat it as if it were a hexavalent element. Benzene  $C_6H_6$ , Schema 185 is in the phenyl series what methane  $CH_4$  is in the methyl series."

Fig. 17 compares Loschmidt's 1861 structures of toluene, phenol, and anisole, and Fig. 18 those of benzyl alcohol, benzaldehyde and benzoic acid with Kekulé's of 1866 and 1867. Fig. 19 shows how correctly Loschmidt depicted the cinnamic moiety; it took chemists many years to ascertain that the double bond was indeed *trans*. It is fitting that the Austrian postal service chose to show the structure of cinnamic acid on the Loschmidt stamp.

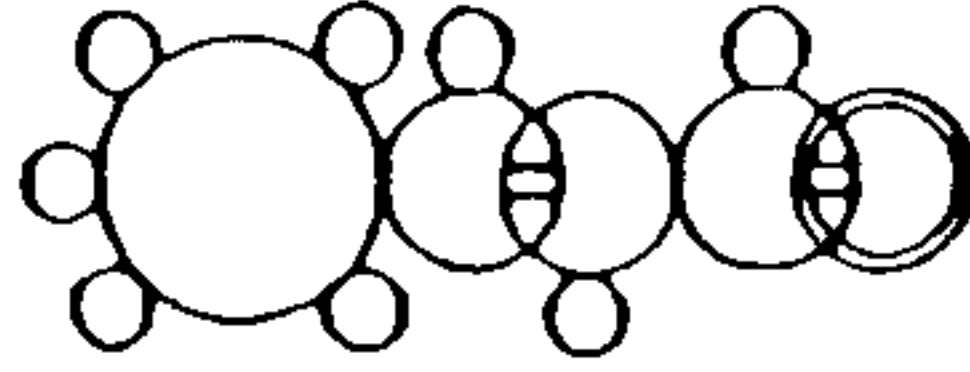
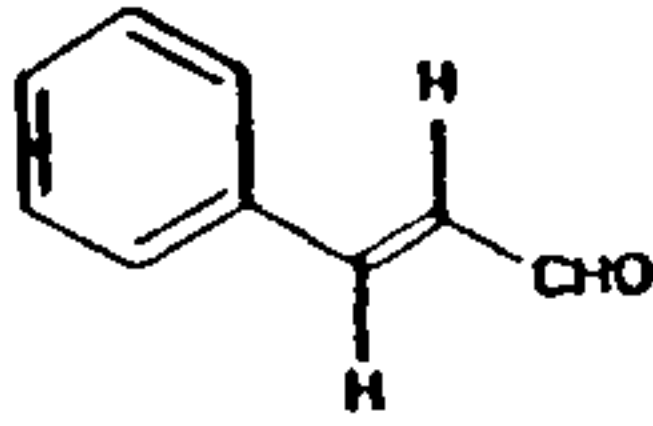
Fig. 20 shows Loschmidt's Schema 228 for aniline, compared to Kekulé's. Phenylenediamine (Fig. 21) is particularly interesting because Loschmidt wrote that "*just looking at Schema 229 shows the possibility of isomeric modifications*," presumably *ortho* and *meta*. Schiemenz<sup>22</sup> suggested that Loschmidt's modifications must have been phenylenediamine and phenylhydrazine. In his chapter on isomerism, Loschmidt had differentiated between isomers "im weiteren Sinne", like phenylenediamine and phenylhydrazine,

Figure 18.  $C_7^{VIII}$  benzyl.

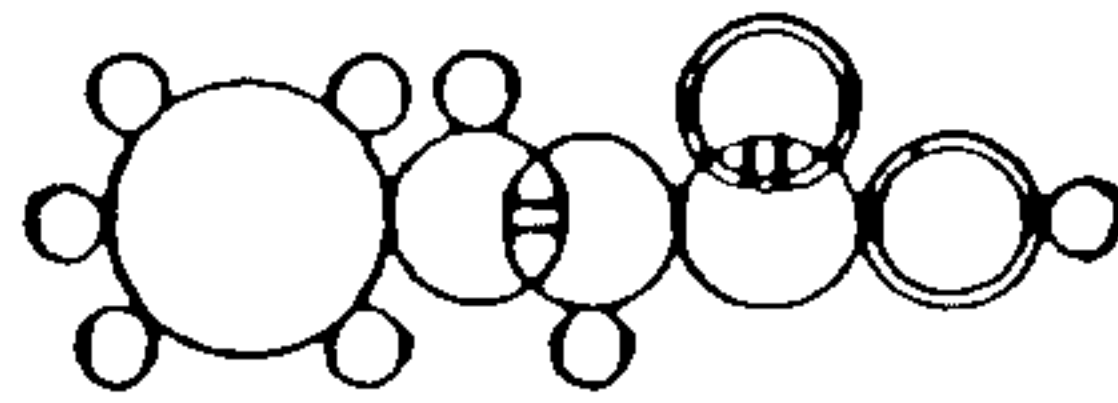
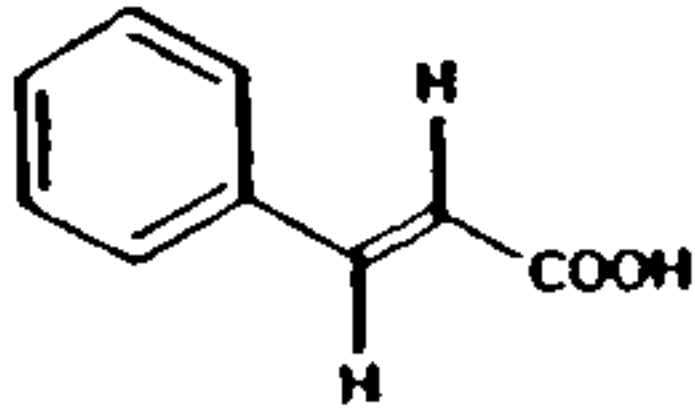
Cinnamyl alcohol



Cinnamaldehyde

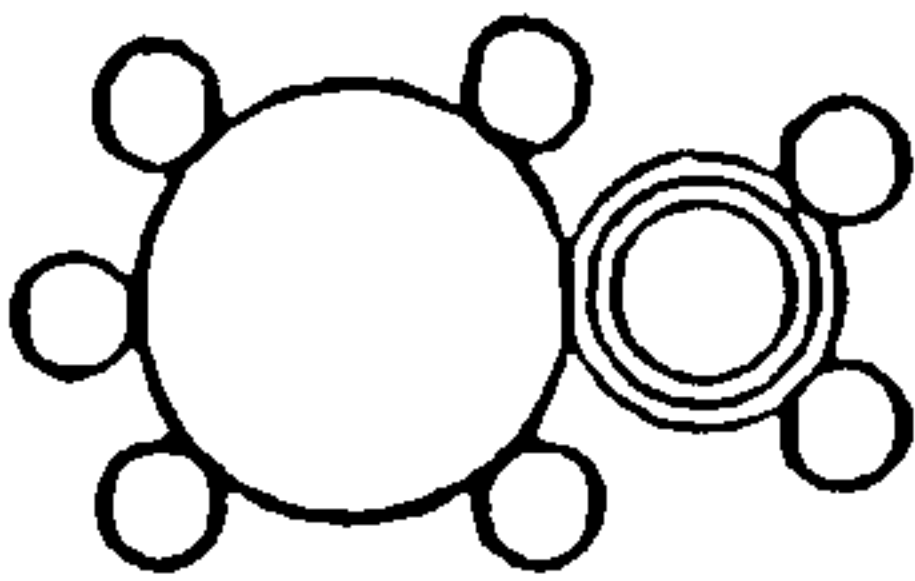


Cinnamic acid

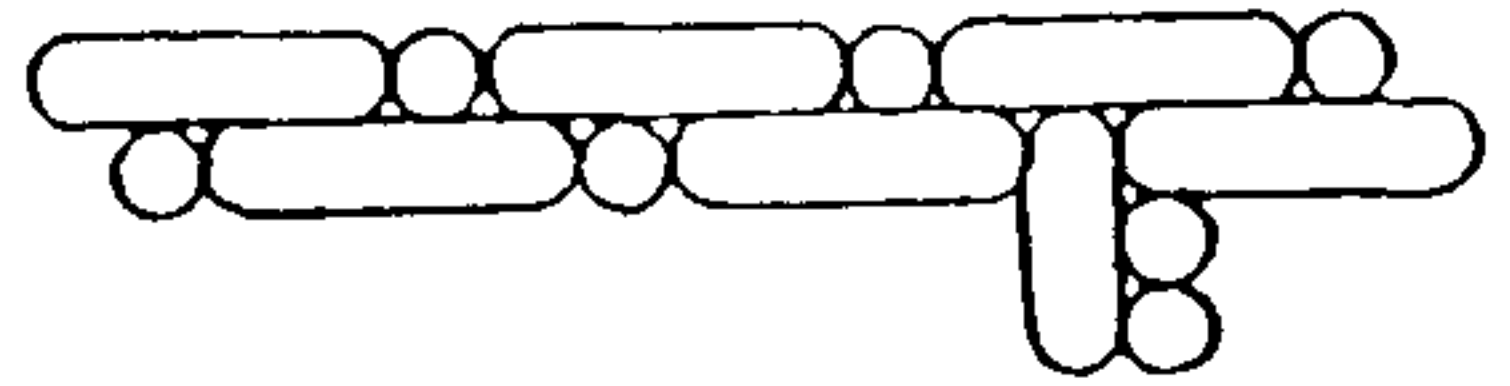
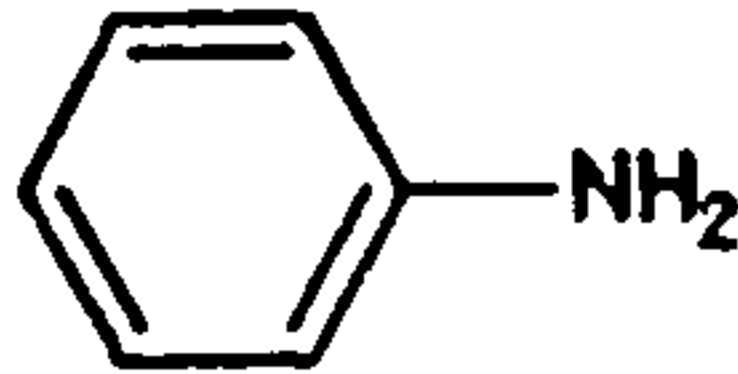


Loschmidt 1861

Figure 19. Cinnamic derivatives.



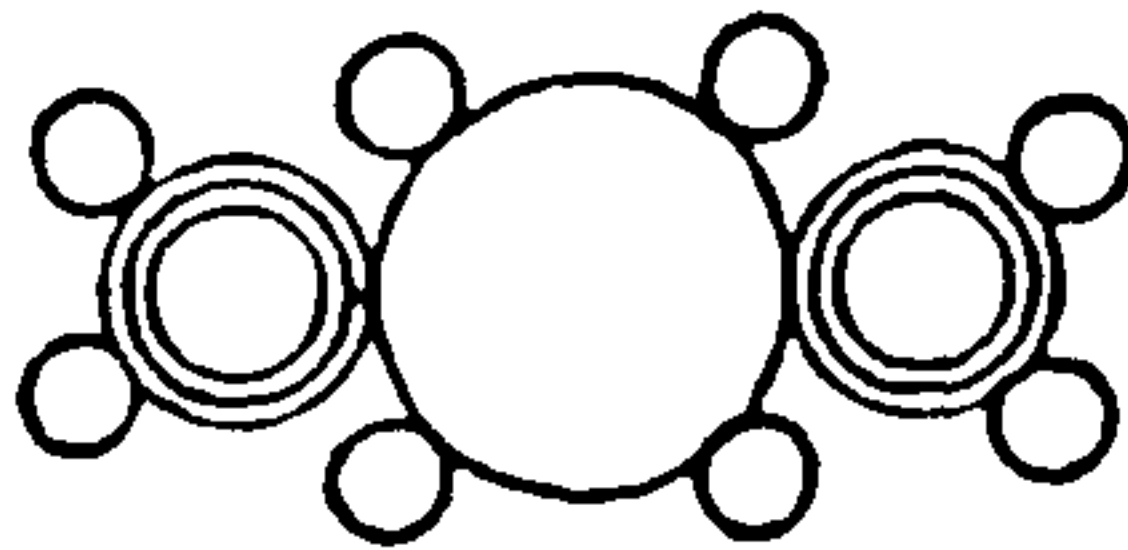
LOSCHMIDT 1861



A. KEKULÉ, LEHRBUCH DER  
ORGANISCHEN CHEMIE 1866  
CHEMIE DER BENZOLDERIVATE 1867

Figure 20. Aniline.

Schon der Anblick des Schemas zeigt die  
Möglichkeit von isomeren Modificationen.



Schema 229

Figure 21. Phenylenediamine.

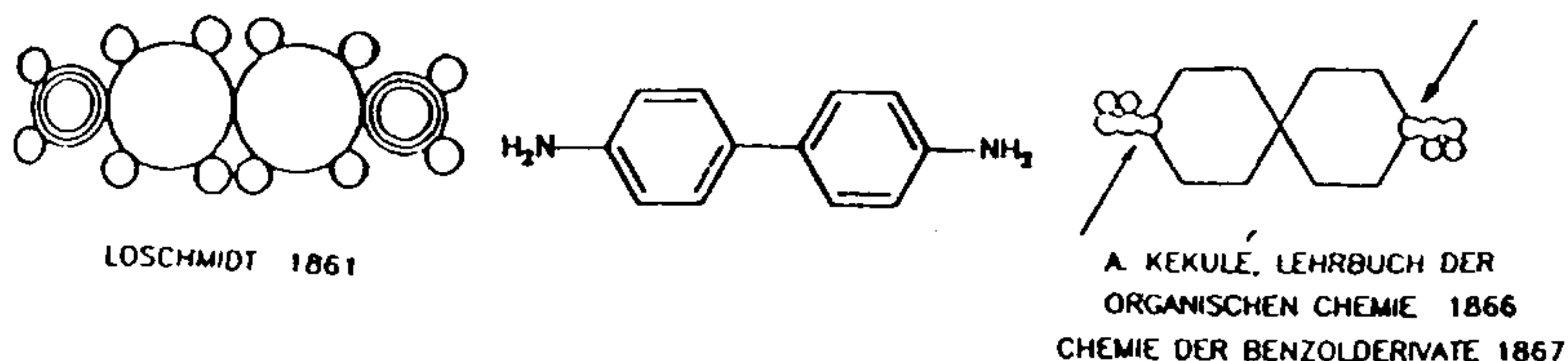


Figure 22. Benzidine.

and isomers "im engem Sinne", like o-, m- and p-phenylenediamine. With the latter<sup>23</sup>, "we will just point to the possibilities..." If Loschmidt had really considered the possibility of phenylhydrazine which was first made 14 years later, he would surely have referred to this as an isomer "im weiteren Sinne".

Figs. 22 and 23 show Loschmidt's and Kekulé's structures of benzidine and benzenesulfonic acid juxtaposed. In 1866–7, Kekulé still believed<sup>24</sup> that benzene might be a hexagon with *hydrogen* at the corners, and so substituents break the rings, as shown.

Most chemists today believe that the benzene hexagon structure with *carbon* in the corners is Kekulé's structure. But Schiemenz has shown<sup>25</sup> convincingly that "the formula which more than a century later is still commonly called *the Kekulé formula* is, to the best of our present knowledge, due to Ladenburg."

Reading Anschütz' discussion<sup>12</sup> of the relationship between Loschmidt and Kekulé, one comes to the conclusion that to Anschütz, the benzene model came from both, with Kekulé's great contribution being the cyclohexatriene concept.

Fig. 24 shows how Loschmidt depicted two of many heterocyclics, 1,4-diphenylpiperazine (Schema 237) and the aromatic chloro-1,3,5-triazine (Schema 239) with two anilino moieties; we don't know why Loschmidt drew chlorine so oddly.

Schiemenz<sup>18</sup> maintains that Loschmidt looked on benzene as a ball, not as a monocyclic six-carbon ring. Yet in his essay on gas laws<sup>26</sup>, Loschmidt stated that we must give molecules a form and have no choice but the ball, even though this is not correct, because molecules of all gases consist of more than one atom. Studying Loschmidt's aromatic structures shown in Figs. 16 through 24 makes it hard to believe that he thought of benzene as a ball. But suppose he did; the fact is that Loschmidt's structures and the consideration leading to these allow us to understand the structures and to decide today which are correct and which are not. With Kekulé's formulae of 1861, this is impossible.

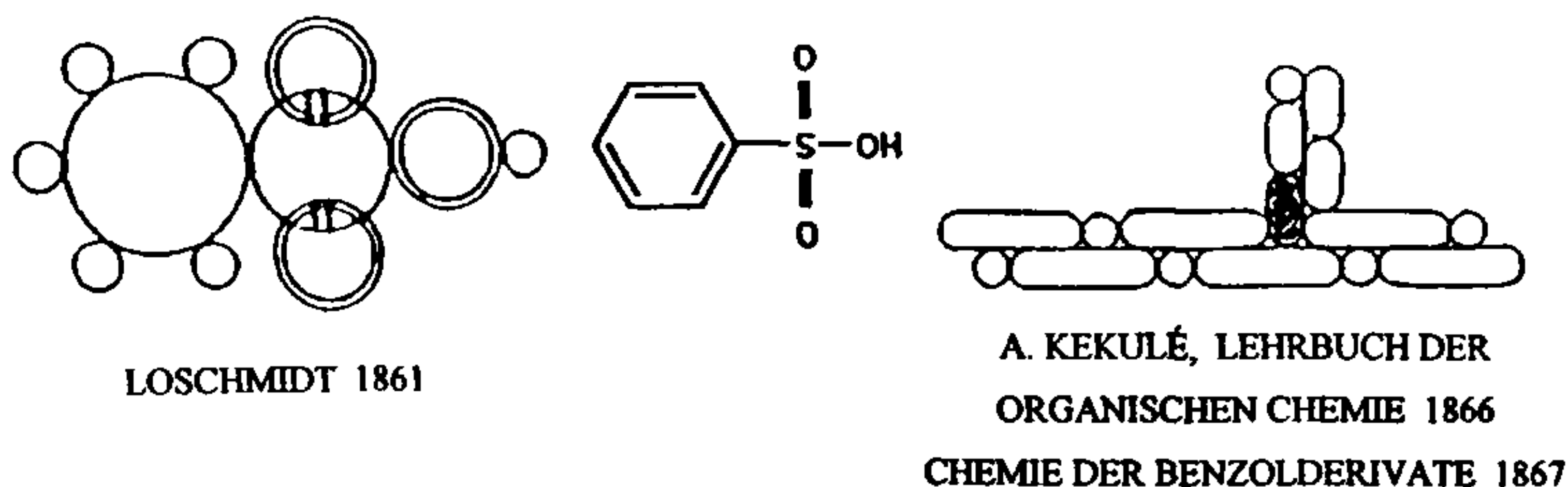


Figure 23. Benzenesulfonic acid.

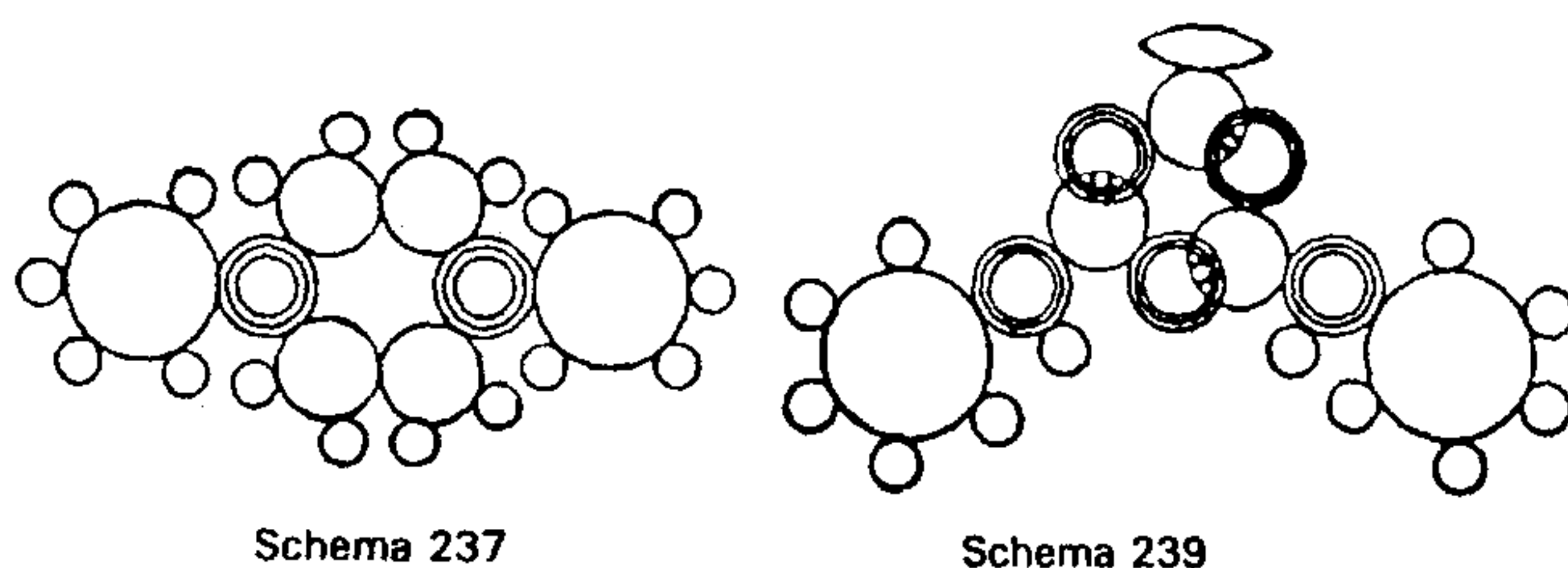


Figure 24. Heterocyclics.

This leads to the interesting question: Did the cyclic structure of benzene come to Kekulé in a dream (Fig. 25)? Perhaps so — to paraphrase Wotiz<sup>27</sup>, dreams do not require footnotes. If he really had that dream, it was probably based on the cyclic structures he had seen in Loschmidt's book of 1861.

In 1980, Klaus Hafner<sup>28</sup>, the director of the Kekulé Museum in Darmstadt, eulogized Kekulé's brilliant discovery of the cyclic structure of benzene:

...again Kekulé succeeded brilliantly. His irresistible desire for clarity and his unusual power of imagination again helped. Basically the benzene formula is a logical conclusion from structural theory. Today it seems obvious, but over a hundred years ago it was an extraordinary mental leap, comparable to the intellectual effort once necessary before man could exchange sled runners for the wheel. *The idea that a hydrocarbon might have a circular structure was totally foreign to chemists of that time. The circle was the symbol for the indivisible, the atom.* [emphasis supplied]

But in 1967, Ferdinand Kirchhof<sup>29</sup> wrote: "The idea that a compound might have a circular structure was totally foreign to chemists of that time. The circle was the symbol

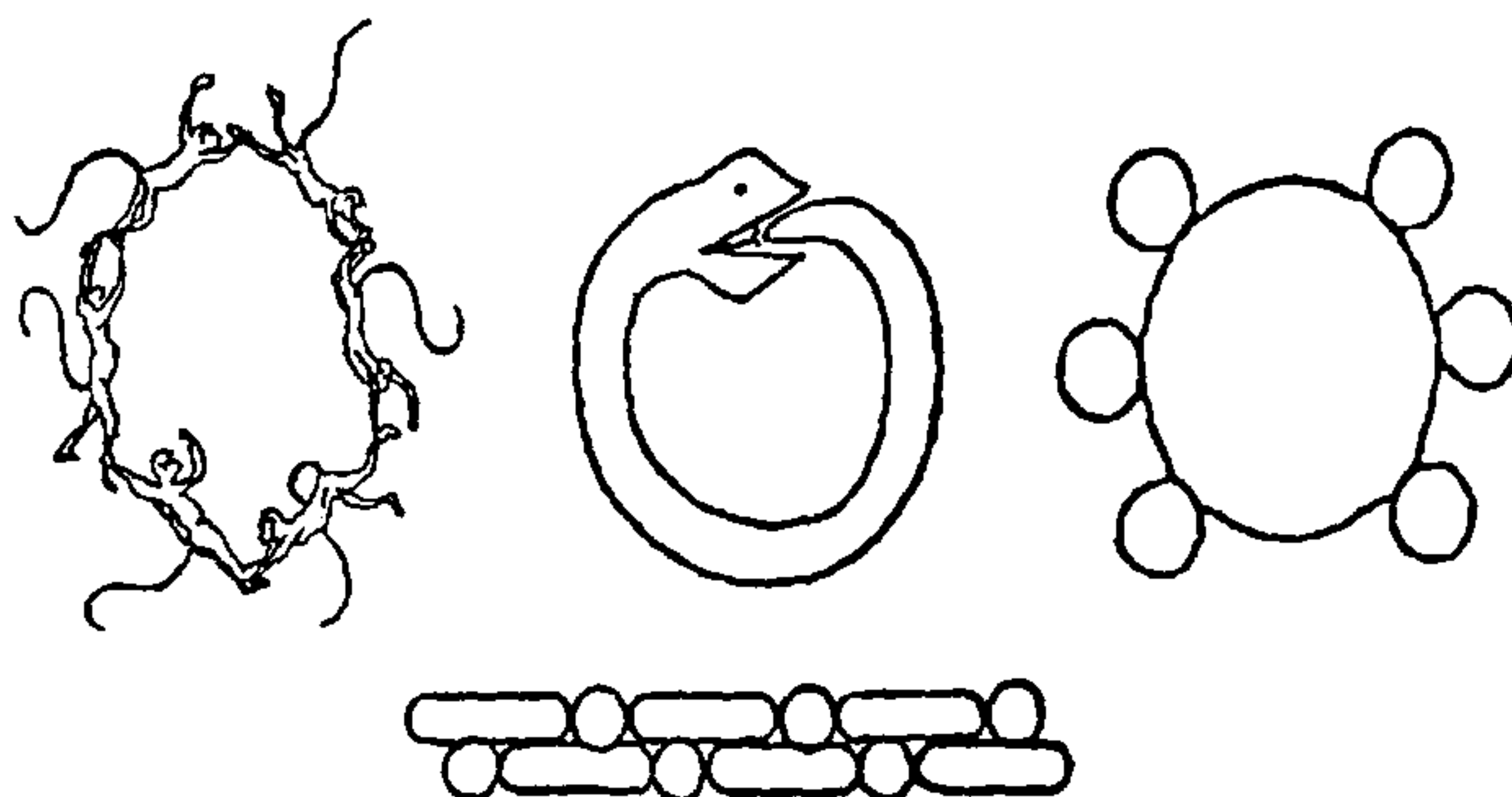


Figure 25. Kekulé's dream.

for the indivisible, the atom, and the merit of having depicted the  $C_6^{VI}$  nucleus as a circle belongs unquestionably to Loschmidt." Loschmidt or Kekulé?

Schiemenz<sup>30</sup> has claimed that Loschmidt's *Chemische Studien* was well-known in the 19th century. Certainly Kekulé and Erlenmeyer and H. Kopp, who reviewed<sup>31</sup> it briefly, knew it, but before Anschütz' work beginning in 1912, there were only three references to it — two disparaging, brief footnotes in Kekulé's papers and Kopp's cursory review. We know of no other citations in the 19th century, not even from Austrian chemists. If indeed chemists knew the *Chemische Studien*, they may have "borrowed" from it without bothering to cite it!

What if? What if Kekulé had pointed to the merits of *Chemische Studien* — that Loschmidt's *Constitutions-Formeln* were superior to the rational formulae used by chemists hitherto? The understanding of chemical structures would have been advanced by decades. We have all been the losers.

Loschmidt must have been deeply discouraged by his complete failure to arouse any interest in his attempt to show the shape of molecules. He shifted most of his attention to physics, where, by calculating the Loschmidt Number, he showed the size of the molecules — the second aspect of the main purpose of his work, "to provide a better understanding of the constitution of matter."<sup>3</sup>

The importance of this work in physics was recognized. His good friend, Ludwig Boltzmann, said in his obituary of Loschmidt<sup>32</sup>: "*His work (in physics) forms a mighty cornerstone which will be visible as long as science exists.*"

Boltzmann did not know the *Chemische Studien* and actually Loschmidt's work included *two* cornerstones. For Wiswesser<sup>2</sup> was right when he wrote "that tiny book of 1861 was really the masterpiece of the century in organic chemistry."

NB: I would like to thank Prof. Dr. Christian R. Noe and Dr. Robert Rosner for archival help and many stimulating discussions.

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# RICHARD ANSCHÜTZ, ARCHIBALD SCOTT COUPER, AND JOSEF LOSCHMIDT

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Milwaukee, Wisconsin

## 1. TWO GREAT HISTORICAL DISCOVERIES OF RICHARD ANSCHÜTZ

Chemists are explorers. We do not know or remember every one, but the names of two men, one a Scot and the other an Austrian, who made major discoveries on our journey to understand chemistry were rescued from oblivion by the persistence of the German chemist, Richard Anschütz (1852–1937).

Anschütz was a student of August Kekulé, became his secretary and then his successor as professor of organic chemistry at Bonn University, and wrote a detailed two-volume biography<sup>1</sup> of Kekulé published in 1929.

During his preparation for the biography, Anschütz made two discoveries which called into question the two great pillars on which Kekulé's fame rests.

One of these, based on a paper<sup>2</sup> published by Kekulé in May of 1858 showed that carbon is tetravalent and that one carbon atom can be linked to another carbon atom. The latter idea was quite revolutionary at the time, and Kekulé's most famous papers were this one and his publication<sup>3</sup> in 1865 of the structure of benzene as a ring of six carbon atoms, an idea which Kekulé claimed twenty-five years later had come to him in a dream.

## 2. ANSCHÜTZ AND COUPER

Richard Anschütz first came across the work of Archibald Scott Couper<sup>4</sup> when he began studying the reaction of salicylic acid with phosphorus pentachloride. Couper had worked on this while an assistant to Adolphe Wurtz in Paris and had published a paper<sup>5</sup> claiming that he obtained a phosphorus-containing compound which boiled around 290° C. Anschütz knew that Kekulé had tried more than twenty times and stated<sup>6</sup> that he had never been able to repeat Couper's work. Others had also tried, under varying conditions, but had failed. Yet, Anschütz and one of his students, George Dunning Moore, repeated the work and discovered that, in fact, Couper was correct.<sup>7</sup>

About twenty years later, while preparing his biography of Kekulé, Anschütz again came across Couper's name on a paper entitled "On a New Chemical Theory". This had been presented in Paris by Jean Baptiste Dumas and published in the *Comptes rendus* in June 1858<sup>8</sup>. In this paper, which was soon forgotten, Couper proposed the tetravalence of carbon and the linking of carbon atoms very much as Kekulé had published one month earlier.

Realizing that Couper had worked quite independently of Kekulé, Anschütz wanted to learn more about this remarkable chemist and turned to the *Edinburgh New Philosophical Journal* of 1858 in which Couper had published<sup>9</sup> his work on salicylic acid in greater detail. He was astonished to find the first formulae with connecting lines indicating the union of atom with atom, the first formulae to which the word "structural", as we know it, could be applied.

Anschütz knew that Kekulé had attacked Couper's claims very strongly in a two-page article<sup>10</sup> published in the *Comptes rendus* in August of 1858. Kekulé had ended his paper by asking Professor Dumas to take note of his complaint. In his biography of Kekulé, Anschütz published<sup>11</sup> an even stronger letter which Kekulé had written to Wurtz:

"As a matter of principle, I will never claim priority for theoretical views as long as that can be avoided. Also, I will not, à la Couper, sound a big horn to proclaim my views as a 'nouvelle théorie chimique'. I will leave it to posterity and the legal sense of others to establish whether the views belong to me and to what extent."

Wurtz' own judgement of Couper's formulae was ambiguous, and Anschütz stated<sup>12</sup> in his biography of Couper that Wurtz should, in fairness, have taken the opportunity to point out that Couper had given him the manuscript, which was not published until June, some time before Kekulé's paper had appeared. Wurtz failed to do that.

### 3. WOODWARD AND COUPER

My own first encounter with the work of Couper came in 1948 through one of the greatest chemists of our time, Robert Burns Woodward, who later wrote:

"In 1858, Archibald Scott Couper was a 27-year-old Scotsman, studying chemistry in the laboratory of Adolphe Wurtz in Paris. He had toyed with philosophy and architecture(!) before settling down to chemical studies. Having pursued the latter for, I believe, something on the order of little more than a year, he prepared a paper entitled *On a New Chemical Theory*, which, after some delay, was published in the *Comptes rendus* of the French Academy of Sciences. In that literally astounding paper, one may see presented, for the first time, *structural formulae*, identical with those we use today — and these are, of course, the most fundamental theoretical tools of organic chemistry.

Now, August Kekulé is rightly given credit for his recognition of and insistence upon the quadrivalency of carbon, and for his brilliant later proposal of the structure of benzene. [Unfortunately, R.B. Woodward did not know of the work of Loschmidt.] But he was *not*, as many believe, the father of structural chemistry. Indeed, in his famous 1858 paper "*On the Constitution and Metamorphoses of Chemical Compounds and the Chemical Nature of Carbon*", he makes very clear his belief at that time that chemical substances adopted diverse structures in response to the influence of attacking reagents; and for many years thereafter, he continued to use, in his own papers, the cumbersome and often obscure "type" formulae of Gerhardt and Laurent. He was, in truth, too much under the influence of the theoretical and physical chemists of the time, who were inordinately opposed to the idea of fixed chemical structure — so much so that, until 1886, the infant *Berichte d. Deutschen Chemischen Gesellschaft*, born in 1868, would

only print structural formulae using dotted-and-dashed lines; the use of solid lines to represent nearest-neighbor relationships would have imputed too much reality to an hypothesis which leading theorists of the day simply would not accept.

So, Archibald Scott Couper deserves recognition for the introduction of structural formulae as we know them..." Woodward then continued: "Now, Couper has received little credit for his brilliant contribution, no doubt largely because not long after his paper was published, he returned to his mother's home in Scotland, went mad, and played no further role in chemistry."<sup>13</sup>

#### 4. CRUM BROWN'S COUPER QUEST

Couper would not have received Woodward's or anyone else's credit had it not been for the intense interest of Richard Anschütz and the persistence and painstaking investigation of Professor Alexander Crum Brown of Edinburgh. Anschütz began to make inquiries about Couper in 1903, writing to his friend, Heinrich Debus, who had been a chemistry professor at the Royal Naval College, Greenwich. In 1906, Debus enlisted the help of Crum Brown, who wrote many letters trying to find out details of Couper's life, his family and his final illness.<sup>14</sup>

A chance comment made by Sir James Dewar in a note written early in 1906, "*It is like a dream to me, as if I had been told that he (Couper) had to be put into an asylum*", led Crum Brown to inquire of the Secretary of the Board of Lunacy for Scotland. He replied that indeed Couper was admitted to a mental institution in 1859, was released and shortly afterwards again admitted, and was finally discharged in 1862, to the care of his mother in Kirkintilloch in Scotland.

With that information, Crum Brown was able to locate several relatives of Couper and to obtain many details and photographs, which he sent to Debus to be forwarded to Anschütz. In reply, Anschütz wrote<sup>14</sup> on June 8, 1906:

...Engaged for years past with the compilation of a comprehensive biography of my many years' chief and venerable friend August Kekulé I studied some time ago for the first time Couper's original papers and I was astonished at the lucidity and the daring of his views regarding the structure of the substances obtained by the action of phosphorus pentachloride upon salicylic acid. Previously in 1885, I had unfortunately contented myself with a miserable abstract, in Liebig's Annalen, of Couper's Salicylic Acid paper. ... 'Mein Gott', I said to myself, 'why did not Couper continue his work: he was, at the time, decidedly freer than Kekulé was from preconceived ideas; with such penetration, what might he not have been able to achieve; he must have died early.'

From an unpublished letter to Crum Brown dated July 22, 1906 we learn that he had received information from several sources:

"Highly Respected Colleague! You can hardly imagine how happy I am to have your letter with its strange and interesting enclosures. For a long time now, I couldn't tear myself away from looking at the photo of Archibald Scott Couper. How tragic his life. His forehead is magnificent, the expression on his face one of melancholy seriousness. ... I have had news from Lieben in Vienna about Couper, whom he met in Wurtz' laboratory. Ladenburg also wrote to me about Couper. Wurtz had told him that he had given Couper's paper about a new theory to Balard because he (Wurtz) was at that point not a member of the Academy. He (Wurtz) let it slide a little, and so Kekulé's paper appeared earlier. Because of this, Couper was very angry, he questioned Wurtz and became insulting. Wurtz would not put up with that and dismissed him from his laboratory, etc."

In 1909, Anschütz published two papers on Couper, one in English<sup>4b</sup> and the second in German,<sup>15</sup> giving details of his life and a critical examination of his published papers. He ended:

“In the history of organic chemistry, the sorely tried Archibald Scott Couper deserves a place of honour beside his more fortunate fellow-worker, Friedrich August Kekulé.”<sup>16</sup>

The collaboration between Anschütz and Crum Brown is described in a most readable and interesting essay entitled “The Couper Quest”<sup>14</sup> written by Leonard Dobbin, an associate of Crum Brown. This gives the details of how Crum Brown found out about Couper’s life, illness and death. Dobbin cited much of the original correspondence<sup>17</sup> between Anschütz, Crum Brown, and others who helped uncover this mystery. Very significant is a letter from an old friend of Couper’s, Geheimrath Gustav Berring in Coblenz, who wrote to Crum Brown in July 1906:

“Couper afterwards wrote to me from Paris that he had made a discovery which Professor Kekulé in Heidelberg also claimed for himself, although wrongly, since priority undoubtedly belonged to him (Couper).”

Clearly Couper believed that he had written his paper before Kekulé’s, and it certainly seems that he was correct in this.

Anschütz was still alive when Dobbin was working on “The Couper Quest,” and on December 19, 1931, in reply to a letter from Dobbin, he wrote:

“For Crum Brown’s successful investigations about Couper’s life, I was only the catalyst. Crum Brown was a doctor of medicine and had the idea to check with insane asylums about Couper; in that he succeeded. ... I noted with pleasure that the Scots celebrated Couper’s 100th birthday from an essay ‘A.S. Couper of Kirkintilloch: A Remarkable Scots Scientific Centenary’ in the Journal of the Society of Chemical Industry of May 8, 1931. To my deep regret, nothing was said therein about Crum Brown’s work to discover Couper’s fate.”

Anschütz was not one to blow his own horn.

## 5. ANSCHÜTZ AND LOSCHMIDT

Anschütz clearly felt that Couper had not been well-treated by Kekulé or Wurtz. This may have made him particularly curious about the work of Josef Loschmidt, whose name he found, linked with that of Crum Brown, in a note in Kekulé’s first paper with a circular structure of benzene. The task of discovering and making public the astounding work of this unknown chemist fell to Anschütz alone.

Reading Kekulé’s seminal paper,<sup>3</sup> he came across a footnote saying “*Elle me parait préférable aux modifications proposées par M M Loschmidt et Crum Brown,*” i.e.: “This seems to me preferable to the modifications proposed by Loschmidt and Crum Brown.” Of course, Anschütz, having worked so closely with Crum Brown, knew of his chemistry, but Loschmidt he knew only as a well-known physicist who had calculated the Loschmidt Number. What was his chemical work?

## 6. LOSCHMIDT'S "CHEMISCHE STUDIEN"

Anschütz found an abstract<sup>18</sup> of a book by Loschmidt in *Liebig's Jahresbericht* of 1861, but this 38-word summary, written by Hermann Kopp, really gave no inkling what the chemistry was all about, and at first, he could not find Loschmidt's book. However, eventually Franz Deuticke, an antiquarian bookseller in Vienna supplied a copy, and Anschütz was staggered when he read it.

In 1861, the very year that Loschmidt published his *Chemische Studien*<sup>19</sup>, Kekulé had written on page 157 of his famous *Lehrbuch der organischen Chemie*<sup>20</sup>:

"...one may use *different rational formulae for the same substance*. At the same time, one must also, of course, keep in mind that the rational formulae are only formulae of reactions ('Umsetzungsformeln') and not formulae of constitution ('Constitutionsformeln'), and that *they do not in any way describe the constitution, i.e., the position of the atoms in the compounds.*" [emphasis supplied]

Yet, in the *Chemische Studien*, Loschmidt showed hundreds of *Constitutions-Formeln*, many of them correct. How could Kekulé have failed to recognize the importance of Loschmidt's work?

Kekulé had been scathing of Couper's claims for his work. He clearly had dismissed Loschmidt's structures, preferring his own. Had he actually seen the *Chemische Studien*, or had he merely heard about the structures from a third party? The book was rare, hard to find, and exceedingly difficult to read. The language was highly technical, often including words which Loschmidt coined. The type was small, and the seven foldout plates illustrating the structures were hard to collate with the text and fell apart easily. In order to make Loschmidt's work known, Anschütz undertook a very arduous task. He reformatted the book so that the structures accompany the text, and the re-publication<sup>21</sup> of 1913 in *Ostwalds Klassiker der Exakten Wissenschaften* was very much easier to read.

Anschütz pointed out that Loschmidt's structures of compounds such as acetic acid were far superior to Kekulé's, that Loschmidt was the first to depict a carbocyclic compound, cyclopropane; the first to show a heterocyclic, cyanuric acid, correctly; the first to show ozone as O<sub>3</sub>; the first to depict sugars correctly, etc. Anschütz must have spent many, many months reformatting Loschmidt's book, writing a brief biography and giving detailed footnotes.

Unable to find any concrete evidence that Kekulé had ever had a copy of *Chemische Studien*, Anschütz stated categorically, in a curt nine-word sentence in his footnotes, that Kekulé had not seen it. But, later he discovered a letter written by Kekulé on January 4, 1862 to Professor Erlenmeyer which ridiculed Loschmidt's structures as *Confusionsformeln* — clearly, a play on words — as *Loschmidt's subtitle is Constitutions-Formeln der organischen Chemie*. In his biography, he cited<sup>22</sup> Kekulé's letter and faulted him for not referring to Loschmidt any further. Anschütz believed that Kekulé considered himself almost like the all-powerful witch doctor of Goethe's poem, *Der Zauberlehrling*, and Loschmidt a mere apprentice.

Whereas the investigation of Couper's contributions to chemistry had been easy, the details of his later life took much more digging because of his tragic illness and virtual disappearance from the scientific world. On the other hand, although given short shrift by Kekulé and virtually ignored by chemists of his day, Loschmidt had the good fortune to become well-known as a physicist, helped by two friends, Josef Stefan and Ludwig Boltzmann, in physics. His worth was clearly recognized, he enjoyed a successful career,

and his work in physics — particularly the calculation of the Loschmidt Number — ensured his place in scientific history.

## 7. LOSCHMIDT'S MODESTY

Why did he not press claim to the importance of his *Chemische Studien*? We know of only one instance<sup>23</sup> when he asked a colleague to promote this book. In 1862, he asked Professor Alexander Bauer, the grandfather of Nobel Laureate Erwin Schroedinger, to take a few copies of the *Chemische Studien* on his trip to France and England to give to scientific colleagues. Only one, the mathematician Liouville in Paris, showed considerable interest.

Many historians of science have found it difficult to understand how a man who became such a well-known professor of physics and dean of the faculty of science could have been so self-effacing a man. Yet the scientists who knew Loschmidt made many references to this quality. For instance, Professor Franz Exner, Loschmidt's successor at the University of Vienna, wrote at the time of the 100th anniversary of Loschmidt's birth<sup>24</sup>: "So exceptionally good-hearted and modest, Loschmidt was completely devoid of jealousy and took as much pleasure in the scientific successes of others as he did in his own."

Anschütz ended his biography of Loschmidt by pointing to an 1890 paper<sup>25</sup> entitled "Stereochemical Studies I" in which Loschmidt again discussed the structure of benzene. Anschütz pointed out that in this very year in which Kekulé was honored with the *Benzolfest* in Berlin celebrating 25 years of the correct benzene structure, Loschmidt could easily have referred to his own work of four years earlier. But he did not. "Clearly, he remained silent because of the undemanding modesty, which was an integral part of his character. The discovery of *Chemische Studien*, long neglected and forgotten, he left to chance..."<sup>26</sup> and luckily to the efforts of Richard Anschütz, for without him we would know almost nothing about Couper's chemistry and life, and nothing about Loschmidt's chemistry.

A quotation from Winston Churchill comes to mind: "Men occasionally stumble over the truth, but most of them pick themselves up and hurry off, as if nothing had happened." Not Anschütz.

NB: I would like to thank Prof. Dr. Christian R. Noe and Dr. Robert Rosner for archival help and many stimulating discussions.

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