Aleksei Yevgen'evich Chichibabin (1871–1945) and Pyridine Chemistry

Dedicated to the memory of Prof. Dr. Vladimir Ivanovich Galkin (1954–2020), Head of the Butlerov Institute of Chemistry at Kazan Federal University, Russian Federation.

The pyridine ring is viewed as a privileged structure in medicinal chemistry, and is well represented in modern pharmaceuticals, as illustrated by the antihistamine, loratadine (**1**), the antiretroviral compound, nevirapine (**2**), the acetylenic retinoid, tazarotene (**3**), used to treat skin conditions such as psoriasis, and the dihydropyridine calcium channel blockers **4**, used to treat hypertension (Figure 1). In this sesquicentennial of the birth of the great pyridine chemist, Aleksei Yevgen'evich Chichibabin (1871–1945),[1] it is appropriate that this name reaction biography focus on pyridine and its analogues.

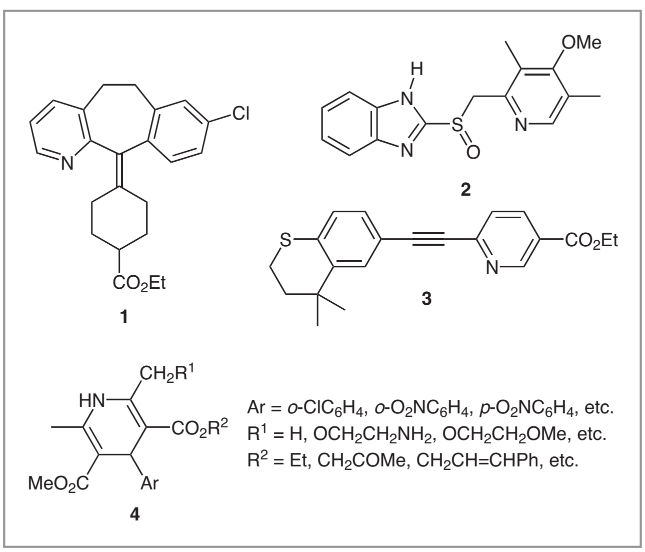

Figure 1 Representative pharmaceuticals containing the pyridine ring

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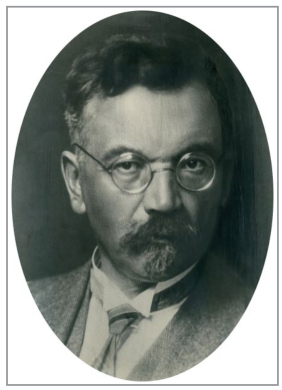
Chichibabin was the first to observe an S_N^H displacement that converted the quite unreactive pyridine nucleus (**5**) into the 2-aminopyridine nucleus (**6**),[2] which is much more reactive towards electrophiles. He also developed an economical, one-pot synthesis of 2,3,5-trisubstituted pyridines **8** from ammonia and monosubstituted acetaldehydes **7**.[3] Although the yields in this reaction are low (typically 20–30%), the simplicity of the reaction, the low cost of the starting materials, and the ability to purify the product by fractional distillation, still render it an important entry into the pyridine ring system. These reactions are summarized in Scheme 1.



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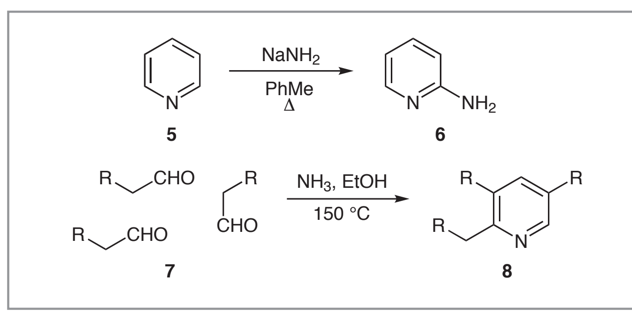

Scheme 1 The Chichibabin amination reaction and the Chichibabin pyridine synthesis

Choose two adjectives to describe Chichibabin's life and career, both 'tragic' and 'traumatic' must be among the top ones that come to mind.

Chichibabin was born in Kuzemino in the Poltava Oblast of the Russian Empire (now part of the Poltava Oblast in Ukraine), the eldest son of Yevgenii Savvich Chichibabin (1837–1876), a collegiate secretary. When Aleksei was three years old, his father moved the family to Lubny, where he took up an appointment as *Zemstvo* (District Council) Secretary. Within two years of this move, Yevgenii Savvich had died, leaving his widow, Natal'ya Petrovna, with six children below the age of ten.

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Despite the financial hardships involved, Natal'ya Petrovna was determined that the younger children should all receive an education, and with Aleksei's older sister, Yevgeniya (b. 1867), she took on extra work to supplement their scant savings. Even so, it was often necessary for the younger children to work to help keep food on the table. In fact, the poverty that characterized his formative years stayed with him until after the October Revolution in 1917.

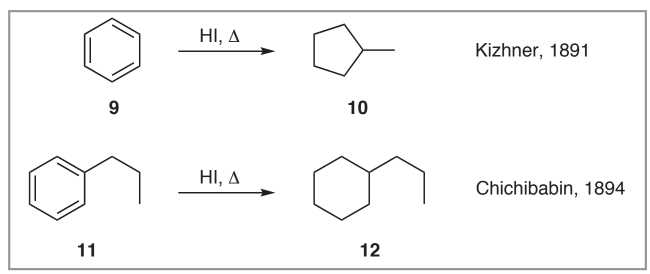
In 1879, Chichibabin entered the Men's Gymnasium in Lubny, but his attendance and performance as a student suffered due to his need to earn money by serving as a tutor. He did graduate from the Gymnasium, and in 1888 he entered the Natural Science Division of the Physics–Mathematics Faculty of Moscow University, where Vladimir Vasil'evich Markovnikov (1837–1904) had rebuilt the organic chemistry program into one of the best in Russia. Pictured are Markovnikov and a group of chemistry professors and lecturers in 1899.

Markovnikov with a group of the chemistry professors and lecturers of Moscow University in 1899

Under the University Statute of 1863, which was probably the most liberal version of the tsarist era, the universities had considerable autonomy: the majority of the power was vested in the University Councils. In 1884, the new University Statute severely curtailed this, and transferred control from the University Councils to the government, which exercised an oppressive oversight. In the spring of 1890, student demonstrations took place, protesting the reform of the Petrovskoe Agricultural Academy (now the Timiryazev Moscow State Agrarian University) to conform with the 1884 statute. Chichibabin was dismissed from the university for his participation in these demonstrations, but he was soon reinstated, and was able to complete his studies without serious interruption.

At the time of Chichibabin's entry into the University, Markovnikov was studying the composition of crude oils—foundational work for the discipline of petrochemistry. Chichibabin was soon working with Markovnikov and his privat-docent, Mikhail Ivanovich Konovalov (1858–1906).

Chichibabin's first project with Markovnikov was to study the Berthelot reduction[4] of propylbenzene with hydriodic acid in a sealed tube. Another Markovnikov student, Nikolai Matveevich Kizhner (1867–1935)[5] had carried out the same reaction with benzene itself (**9**) and found that the product was not cyclohexane, but methylcyclopentane (**10**).[6] In contrast to Kizhner's work, Chichibabin found that the reduction of propylbenzene (**11**) led to propylcyclohexane (**12**),[7] without rearrangement (Scheme 2).



Scheme 2 The Berthelot reductions of benzene and propylbenzene carried out by Kizhner and Chichibabin in Markovnikov's laboratory

Chichibabin graduated with the *diplom* in 1892, and under normal circumstances would have continued his education at Moscow forthwith. But circumstances were not normal. In 1893, the outspoken Markovnikov was ousted from his Professorship when his enemies used an arcane regulation that allowed the university to force compulsory retirement on any academic who had served 25 years since their first appointment. For Markovnikov, this came in 1893.[8]

Markovnikov's Chair was given to Nikolai Dmitrievich Zelinskii (1861–1953), who was on poor terms with Markovnikov (Markovnikov had accused him of unethical practices by carrying out research on Markovnikov's project without notifying him). Zelinskii's antipathy extended to Markovnikov's student, so Chichibabin was left without a formal research mentor. For the next three years, he lived on what he could earn as a private tutor and a journalist reporting on scientific stories. In 1895, Professor Rudnev of the Aleksandrovskii

College of Commerce invited him to become Assistant in the laboratory, but he was not approved for a permanent position and was forced to leave a year later. At the same time, he continued his scientific work, working on analytical techniques for industry, in the laboratory of the *Society for the Promotion of the Manufacturing Industry*, where he became Assistant Head of the laboratory.

Chichibabin's return to financial security came in 1896, when Konovalov was appointed to the Chair at the Moscow Agricultural Institute and made him the Head of the chemistry laboratory. In 1901, he was appointed Privat-Docent at Moscow University, where he remained until 1911. In 1905, he accepted the position of Chair of Inorganic Chemistry at Warsaw University with the rank of Extraordinary Professor, but he returned to Moscow as Director of the Moscow Agricultural Institute less than a year later because he found the facilities and atmosphere there totally incompatible with his research. In 1908, he was appointed Professor of General and Organic Chemistry at the Moscow Higher Technical School (now Bauman Moscow State Technical University), where he remained until 1930 as either Professor or Dean.

Chichibabin with his students in the laboratory of organic synthesis at the Higher Technical School, spring semester 1914

Even as a professor, Chichibabin retained the progressive ideals of his youth; in 1908, the police took note of regular meetings of anti-government individuals in his home, where they also found banned revolutionary literature. For whatever reason, his involvement was kept secret, and he retained his position. Then, in 1911, he resigned his position at Moscow University in solidarity with other progressive-minded colleagues (among them, future Academicians Kliment Arkad'evich Timiryazev (1843–1920), Pyotr Nikolaevich Lebedev (1866–1912), and Vladimir Ivanovich Vernadskii (1863–1945) who were protesting the reactionary policies of Lev Aristidovich Kasso (1865–1914), the Minister of Education. Although Chichibabin resigned from his position at Moscow University, he retained his position at the Higher Technical School.

With the advent of World War I, Chichibabin turned his attention to the nation's need for a reliable supply of pharmaceuticals. A 1904 trade agreement with Germany on coaling Russian naval vessels[9] had included a provision precluding Russia from refining coal tar.[1b] This was an important raw material for the pharmaceutical industry, giving Germany a monopoly in Russia on synthetic pharmaceuticals. With the war cutting off the supplies of these compounds from Germany, Chichibabin helped to organize the Moscow Committee for the Development of the Chemical Pharmaceutical Industry.

He also served as the first Head of the Committee. As part of his work for the committee, Chichibabin organized pilot plant laboratories for the isolation of alkaloids—morphine, codeine, atropine and caffeine—at both the Higher Technical School and the Shanyavskii People's University in Moscow, and during this time he also taught at both institutions.[10] In addition, he organized the manufacture of synthetic analgesics and antipyretics such as salicylic acid, aspirin, phenacetin, and phenyl salicylate. His efforts were credited with saving the lives of thousands of Russian soldiers during the war.

Two revolutions took place in Russia during 1917: the February Revolution, which led to the abdication of the Tsar, and the October revolution (the Bolshevik revolution), which began the Soviet era of Russian history. It was followed by a bloody civil war that did not end until 1923, five and a half years later. Chichibabin's loyalties were to Russia, and not to any political party, so he had no problem shifting his allegiance to the new regime. He continued his efforts to build the Russian pharmaceutical industry of the State Board of Chemical and Pharmaceutical Plants and headed the Chemical–Pharmaceutical Institute. By the time Chichibabin left Russia, his efforts and foresight had assured that Russia had fully functional chemical and pharmaceutical manufacturing industries.

During the civil war, shortages of such essentials as food, shelter and clothing became endemic in Russia after almost a decade of continuous warfare. During this time, Chichibabin wrote his textbook, *Osnovnye nachala organicheskoi khimii* [*Fundamentals of Organic Chemistry*],[11] trading a few pages at a time to the publisher in return for additional ration cards for food. This book became the dominant organic chemistry textbook in Russia, going through seven Russian editions, and was eventually translated into seven other languages.

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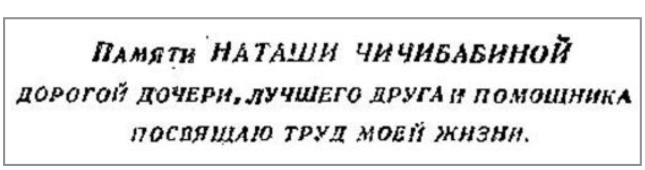
By 1925, Chichibabin had become an elder statesman of organic chemistry—especially synthetic pharmaceutical chemistry—in Russia. That year, he won the Greater Butlerov Prize of the USSR Academy of Sciences, and in 1926 he received the first Lenin Prize for chemistry. In 1927, he was elected a Corresponding Member of the USSR Academy of Sciences, and a Full Member (Academician) in 1929. In 1927, he and Vladimir Nikolaevich Ipatieff (1867–1952) were among the Russian scientists invited to participate in 'Russian Science Week' in Berlin.

In 1910, at the age of 39 years, Chichibabin became father to a daughter, Natal'ya Alekseevna (Natasha, 1910–1929), pictured here. He doted on his daughter, who chose to follow her father's footsteps into chemistry. As a student at the Technical Institute, she was required to obtain practical training in industry. She was working at the Dorogomilovskii chemical plant in Moscow, where naphthalenesulfonic acids for the dye industry were produced by the sulfonation of naphthalene with oleum at 180 °C. She had been assigned a task for which she had not been trained, operating a sulfonating autoclave. Thanks to the incompetence of the apparatchik supervising her work, there was an explosion that left her severely burned. She spent the next two days in agony before dying of her injuries.[12] Chichibabin dedicated the third edition of his *Osnovnye*, published in 1931, to his deceased daughter (Figure 2).

Chichibabin with his daughter, Natasha



Памяти НАТАШИ ЧИЧИБАБИНОЙ
дорогой дочери, лучшего друга и помощника
посвящаю труд моей жизни.

Figure 2 The dedication in the third edition of the *Osnovnye*. It reads „In memory of Natasha Chichibabina, dear daughter, best friend and helper, I dedicate the work of my life."

Natasha's death devastated her parents and made it impossible for them to remain in Moscow, where the accident had happened because of the incompetence of her supervisor. Her mother, Vera Vladimirovna, drifted into a deep depression. In 1930, Chichibabin was awarded a *komandirovka* (paid study leave) in Paris, where he worked with Tiffeneau. He and his wife left Russia for good in 1930.

Chichibabin spent his first two years in Paris in the laboratory of Marc Tiffeneau at the Hôtel-Dieu. At the same time, Vera Vladimirovna underwent psychiatric treatment to help her cope with the deep depression caused by her daughter's death. After two years, Chichibabin was placed in charge of a special research laboratory in the French pharmaceutical and dye company, the Établissements Kuhlmann. At the same time, he became a consultant to the German pharmaceutical company, Schering AG, and to Roosevelt and Company of New York. In 1931, he was offered a small laboratory in the Collège de France, and here he spent the remainder of his career.

Chichibabin's time in Paris was not always happy. He was homesick for Russia, but the political situation there made him wary of returning, despite the many letters he received from high-ranking Soviet scientists begging him to return and assuring him of his welcome. Stalin's purges of the late 1930s suggest he was right. Chichibabin never returned to Russia, and in 1936 he was stripped of his Soviet citizenship and his membership in the USSR Academy of Sciences, with six members dissenting. With the outbreak of World War II, foreigners were denied permission to work in France, so once again Chichibabin fell into straitened circumstances. He died in Paris the day the war ended. In 1990, one of the last acts of the USSR Academy of Sciences was to reinstate Chichibabin to Full Membership.

Chichibabin Pyridine Synthesis

In 1896, Chichibabin began his research into the chemistry of pyridine and its derivatives, culminating in seven papers in Russian (*Zh. Russ. Fiz.-Khim. O-va.*)[13] and five in German[14] by 1902. In 1902, he submitted his dissertation for the *Magistr Khimii* (Figure 7) on the reactions of pyridine and quinoline with alkyl halides and the products of thermolysis of the resultant quaternary ammonium ions to give mixtures of α- and γ-alkylpyridines and -quinolines.[15]

Although he submitted his M. Khim. dissertation in 1902, scheduling its defense was problematical in the face of opposition by Zelinskii and his allies. When the defense was finally scheduled (in 1903), Zelinski wrote a negative examiner's report; the comment by Aleksander Pavlovich

Sabaneev (1843–1923), an organic chemist who was Dean of the faculty, is also illustrative of the atmosphere: when Chichibabin rose to defend his dissertation, Sabaneev mocked him as being a 'self-taught man'. At the time, not being associated with a recognized school was a reason to demean, rather than congratulate the student for completing his work despite the absence of a formal research mentor. His relationship with his old mentor had become cold, so even Markovnikov did not give his approval of the work. Chichibabin revised and resubmitted the dissertation, and the degree was finally awarded in 1904. The atmosphere at Moscow in the aftermath of his defense was truly toxic, so six months later he accepted the appointment to the University of Warsaw.

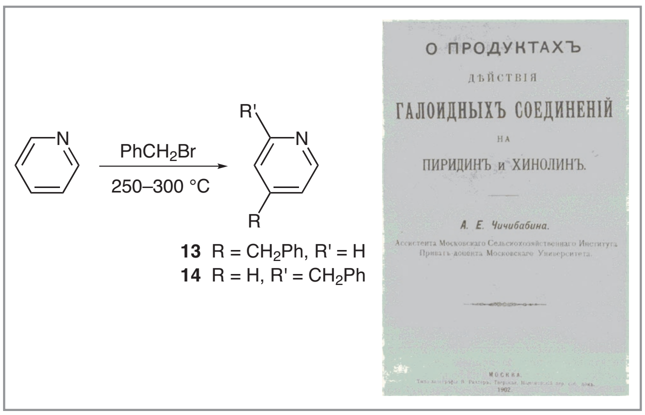
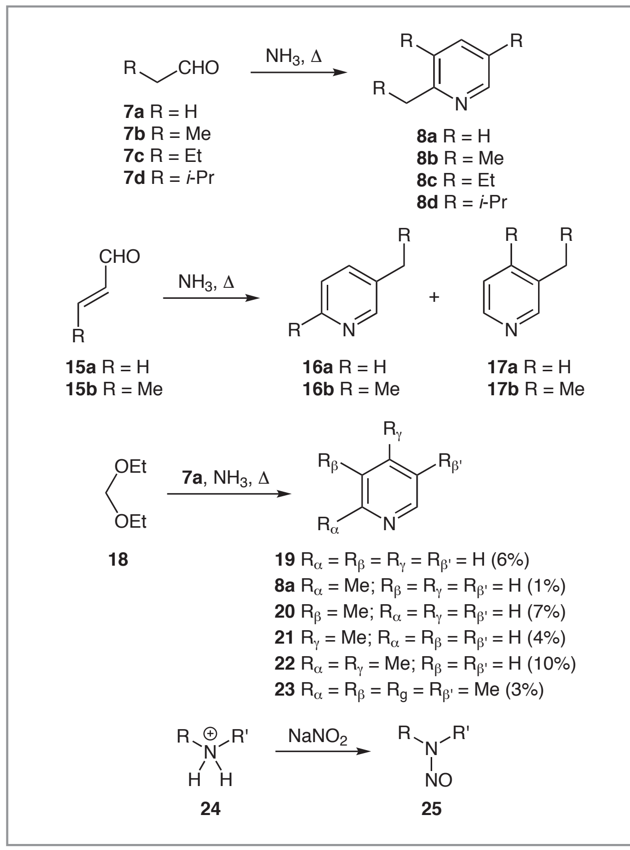


Figure 3 (left) Chichibabin's thermolysis of pyridinium salts and (right) his *M. Khim.* dissertation

In 1905, Chichibabin published his first report of the synthesis of pyridines from aldehydes and ammonia;[3] that same paper carried a footnote[16] that some of the experimental details had been published earlier. It was not until over a decade and a half later before he again entered the field, with five papers in Russian in 1921,[17] and six papers in German in 1924.[18] As part of this project, Chichibabin and his students developed aluminum oxides and hydroxides as catalysts for the reaction.

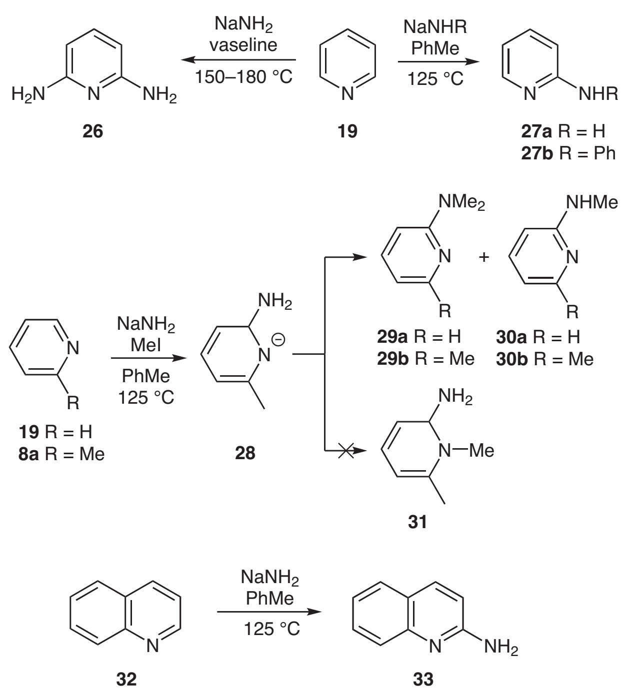
In the later series of papers, Chichibabin and his students were able to expand the scope of the reaction for the preparation of diverse pyridine derivatives (Scheme 3). Thus, using single monosubstituted acetaldehyde derivatives **7a–d** gave the 2-(alkylmethyl)-3,5-dialkylpyridines **8a–d**. The use of a monosubstituted acrolein derivative (**15**) led to the production of 2,5-disubstituted and 3,4-disubstituted pyridine derivatives **16** and **17**. Using acetaldehyde with a formaldehyde equivalent (e.g., the diethylacetal **18**) led to the production of pyridines carrying anywhere from zero to four alkyl groups, as illustrated in Scheme 3. In this reaction, the major product, 3,5-lutidine (**22**) was formed from two equivalents of acetaldehyde and one equivalent of the acetal. The overall yield of pyridines in this reaction was 31%. The reaction also produced secondary amine by-products, and these were removed from the basic pyridines by treating the hydrochloric acid solution of the bases with sodium nitrite, thus converting the secondary amine hydrochlorides **24** into non-basic *N*-nitrosamines **25**. Chichibabin and Oparina[18f] separated the mixture of alkylated pyridines by fractional distillation and then fractional crystallization of their picrates.



Scheme 3 The variations of the Chichibabin pyridine synthesis reported by Chichibabin and his students

Chichibabin Amination

The best-known reaction carrying Chichibabin's name is the amination of pyridines and quinolines with sodium amide in a hydrocarbon solvent.[2] In their initial paper, Chichibabin and Zeide showed that in refluxing toluene around 125 °C, pyridine (**19**) was converted into 2-aminopyridine (**27**), and that in a paraffin solvent at 150–180 °C, a second amino group was inserted, giving 2,6-diaminopyridine (**26**). The mechanism of the reaction begins with the addition of amide anion to the heterocyclic ring to give the conjugate base of a 2-amino-1,2-dihydropyridine (**28**), which the authors sought to trap by means of methylation. The expected product, **31**, was not obtained, but the mono- (**30**) and dimethylaminopyridines (**29**) instead, which showed that the rearomatization by elimination of hydride is faster than alkylation of the anion. The authors also reported the amination of quinoline to give 2-aminoquinoline (**33**). The reactions reported in the initial publication are gathered in Scheme 4.

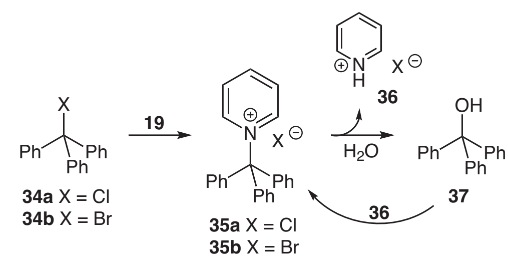


Scheme 4 Representative Chichibabin amination reactions

Chichibabin saw the potential for both pharmaceuticals and dyes based on the pyridine ring system. Consequently, he and his students at Shanyavskii Moscow State University carried out an extensive research program on the exploitation of the reactions of aminopyridines. In 1918, he and his students published twelve papers in this area encompassing 74 pages in the *Zhurnal*.[19]

Triarylmethyl Compounds

In 1900, Russian émigré Moses Gomberg reported the discovery of the triphenylmethyl radical,[20] the first stable free radical. This discovery quickly attracted the interest of Chichibabin, who began a long-term research program into the chemistry of trivalent carbon compounds. His first works involved the synthesis of pyridine derivatives of triphenylmethane. The alkylation of pyridine with a triphenylmethyl halide **34** gave the corresponding salt **35**, but on work-up with water, the pyridinium halide **36** and triphenylmethanol (**37**), presumably by an S_N1 mechanism; treatment of **37** with **36** gave the same salt (Scheme 5).[21] This work was expanded into the study of the structure of 'hexaphenylethane'.[22] In 1912, this work formed the basis of Chichibabin's *Dr. Khim.* dissertation.[23]



Scheme 5 Reactions of triphenylmethyl halides with pyridine

Early on, Chichibabin had come to the conclusion that the correct structure of hexaphenylethane was actually the quinoid dimer **38**. In 1907, he published the synthesis of a violet solid, **39**, that is known today as Chichibabin's hydrocarbon (Figure 4).[24] Among other things, this fascinating compound has C_i symmetry.[25]

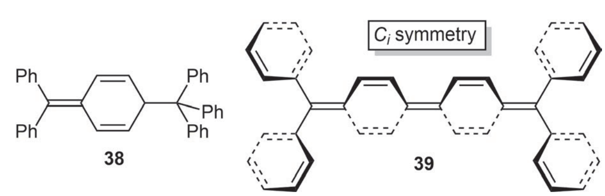
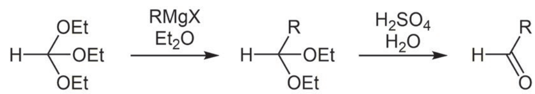


Figure 4 Chichibabin's hydrocarbon

Bodroux–Chichibabin Aldehyde Synthesis

In 1904, Chichibabin and French chemist F. Bodroux published three papers describing the synthesis of aldehydes through the preparation of acetals by the reaction between Grignard reagents and ethyl orthoacetate (Scheme 6).[26]



40 41 42

Scheme 6 The Bodroux–Chichibabin aldehyde synthesis

REFERENCES

(1) For biographical information on Chichibabin, see: (a) I. Marszak *J. Chem. Soc.* **1946**, 760–761. (b) E. Cerkovnikov *J. Chem. Educ.* **1961**, *38*, 622–624. (c) M. Delépine *Bull. Soc. Chim. Fr.* **1946**, 501–510. (d) P. M. Yetveeva *Trudy in-ta istorii estestvoznaniya i tekhniki* **1958**, *18*, 296–356. (e) A. Ye. Zaitseva *Khimiya* **2001**, *16*, 1. (f) E. A. Zaitseva, In *Proceedings of the 5th International Conference on the History of Chemistry: Chemistry, Technology and Society*; I. Malaquias, E. Homburg, M. E. Callapez (Eds.); Sociedade Portuguesa de Quimica: Aveiro, **2006**; 260–273. (g) V. A. Volkov, M. V. Kulikova *Priroda* **1993**, *9*, 122–128. (h) V. A. Volkov, In *Rossiiskie Uchenie i Inzhenery v Emigratsii [Russian scientists and Engineers in Emigration]*; V. P. Borisov (Ed.) In-ta. istorii estestvoznaniya i tekhniki: Moscow, 1993; 40–71. (i) D. E. Lewis *Angew. Chem. Int. Ed.* **2017**, *56*, 9660–9668.

(2) A. Ye. Chichibabin, O. A. Zeide *Zh. Russ. Fiz.-Khim. O-va.* **1914**, *46*, 1214–1236.

(3) A. Ye. Chichibabin *Zh. Russ. Fiz.-Khim. O-va.* **1905**, *37*, 1229–1253.

(4) (a) M. Berthelot *Bull. Soc. Chim. Paris* **1867**, *7*, 53–65. (b) M. Berthelot *Bull. Soc. Chim. Paris* **1868**, *9*, 8–31.

(5) For overviews of Kizhner's work, see: (a) D. E. Lewis *The Wolff-Kishner Reduction and Related Reactions*; Elsevier: Amsterdam, **2019**. (b) D. E. Lewis *Synform* **2017**, *12*, A208–A212. (c) D. E. Lewis *Angew. Chem. Int. Ed.* **2013**, *52*, 11704–11712. (d) V. Suntsov, D. E. Lewis *Bull. Hist. Chem.* **2014**, *39*, 43–52.

(6) (a) N. M. Kizhner *Zh. Russ. Fiz.-Khim. O-va.* **1891**, *23*, 20–26. (b) N. M. Kizhner *Zh. Russ. Fiz.-Khim. O-va.* **1892**, *24*, 450–454. (c) N. M. Kizhner *Zh. Russ. Fiz.-Khim. O-va.* **1894**, *26*, 375–380.

(7) A. Ye. Chichibabin *Zh. Russ. Fiz.-Khim. O-va.* **1894**, *26*, 40–45.

(8) A. F. Platé, G. V. Bykov, M. S. Eventova *Izd. Akad. Nauk SSSR* **1963**, 135.

(9) (a) S. B. Fay *Am. Hist. Rev.* **1918**, *24*, 48–72. (b) L. J. R. Cecil *Am. Hist. Rev.* **1964**, *69*, 990–1005.

(10) V. I. Onoprienko *Stud. Hist. Biol.* **2018**, *10*, 121–131.

(11) A. Ye. Chichibabin *Osnovnye nachala organicheskoi khimii [Fundamentals of Organic Chemistry]*, 3rd ed.; Gos. Izd-vo: Moscow, **1931**.

(12) (a) Yu. I Solov'ev *Vestnik RAN* **1993**, *63*, 516–518. (b) Yu. I. Solov'ev *Tragediheskie sud'by: repressirovannye uchenye Akademii nauk SSSR [Tragic Fates: Repressed Scientists of the Academy of Sciences of the USSR]*; Nauka: Moscow, **1995**, 46–53.

(13) (a) A. Ye. Chichibabin *Zh. Russ. Fiz.-Khim. O-va.* **1901**, *33*, 249–258. (b) A. Ye. Chichibabin *Zh. Russ. Fiz.-Khim. O-va.* **1901**, *33*, 404 –410. (c) A. Ye. Chichibabin *Zh. Russ. Fiz.-Khim. O-va.* **1901**, *33*, 700–707. (d) A. Ye. Chichibabin *Zh. Russ. Fiz.-Khim. O-va.* **1902**, *34*, 130–133. (e) A. Ye. Chichibabin *Zh. Russ. Fiz.-Khim. O-va.***1902**, *34*, 133–137. (f) A. Ye. Chichibabin *Zh. Russ. Fiz.-Khim. O-va.* **1902**, *34*, 137–140. (g) A. Ye. Chichibabin *Zh. Russ. Fiz.-Khim. O-va.* **1902**, *34*, 508–514.

(14) (a) A. E. Tschitschibabin *Ber. Dtsch. Chem. Ges.* **1903**, *36*, 2709–2711. (b) A. E. Tschitschibabin *Ber. Dtsch. Chem. Ges.* **1903**, *36*, 2711–2713. (c) A. E. Tschitschibabin *Ber. Dtsch. Chem. Ges.* **1904**, *37*, 1373–1374. (d) A. E. Tschitschibabin *Ber. Dtsch. Chem. Ges.* **1905**, *38*, 3834–3834. (e) A. E. Tschitschibabin *J. Prakt. Chem.* **1904**, *69*, 310–320.

(15) A. Ye. Chichibabin *O produktakh deistvie galoidnykh soedinenii na piridin I khinolin. [On the products of the action of halogen compounds on pyridine and quinoline], M. Khim. Dissertation*, Moscow; **1902**.

(16) The footnote reads: "Part of the experimental data included in this article and a more detailed literary review have already been published in the Bulletin of the Moscow Agricultural Institute for 1903, Vol. 4, as well as a separate brochure: «N. N. Lyubavin's valeritrine and on the reactions of synthesis of pyridine bases using aldehydes and ammonia.» Moscow (1903)."

(17) (a) A. Ye. Chichibabin *Zh. Russ. Fiz.-Khim. O-va.* **1921**, *54*, 402–411. (b) A. Ye. Chichibabin *Zh. Russ. Fiz.-Khim. O-va.* **1921**, *54*, 411–413. (c) A. Ye. Chichibabin, P. A. Moshkin, L. S. Tyazhelova *Zh. Russ. Fiz.-Khim. O-va.* **1921**, *54*, 413–420. (d) A. Ye. Chichibabin, M. P. Oparina *Zh. Russ. Fiz.-Khim. O-va.* **1921**, *54*, 420–427. (e) A. Ye. Chichibabin, M. P. Oparina *Zh. Russ. Fiz.-Khim. O-va.* **1921**, *54*, 428–446.

(18) (a) A. E. Tschitschibabin *J. Prakt. Chem.* **1924**, *107*, 122–128. (b) A. E. Tschitschibabin *J. Prakt. Chem.* **1924**, *107*, 129–131. (c) A. E. Tschitschibabin, P. A. Moschkin, L. S. Tjaschelowa *J. Prakt. Chem.* **1924**, *107*, 132–137. (d) A. E. Tschitschibabin, M. P. Oparina *J. Prakt. Chem.* **1924**, *107*, 138–144. (e) A. E. Tschitschibabin, M. P. Oparina *J. Prakt. Chem.* **1924**,

107, 145–154. (f) A. E. Tschitschibabin, M. P. Oparina *J. Prakt. Chem.* **1924**, *107*, 154–158.
(19) (a) A. Ye. Chichibabin, V. S. Tyazhelova *Zh. Russ. Fiz.-Khim. O-va.* **1918**, *50*, 483–492. (b) A. Ye. Chichibabin *Zh. Russ. Fiz.-Khim. O-va.* **1918**, *50*, 492–494. (c) A. Ye. Chichibabin, L. S. Tyazhelova *Zh. Russ. Fiz.-Khim. O-va.* **1918**, *50*, 495–497. (d) A. Ye. Chichibabin *Zh. Russ. Fiz.-Khim. O-va.* **1918**, *50*, 497–502. (e) A. Ye. Chichibabin *Zh. Russ. Fiz.-Khim. O-va.* **1918**, *50*, 502–511. (f) A. Ye. Chichibabin *Zh. Russ. Fiz.-Khim. O-va.* **1918**, *50*, 512–519. (g) A. Ye. Chichibabin, M. A. Voron'ev *Zh. Russ. Fiz.-Khim. O-va.* **1918**, *50*, 519–522. (h) A. Ye. Chichibabin, O. A. Zeide *Zh. Russ. Fiz.-Khim. O-va.* **1918**, *50*, 522–533. (i) O. A. Zeide *Zh. Russ. Fiz.-Khim. O-va.* **1918**, *50*, 534–543. (j) A. Ye. Chichibabin, M. P. Oparina *Zh. Russ. Fiz.-Khim. O-va.* **1918**, *50*, 543–548. (k) A. Ye. Chichibabin, L. A. Bukhol'ts *Zh. Russ. Fiz.-Khim. O-va.* **1918**, *50*, 548–552. (l) A. Ye. Chichibabin, E. V. Zatsepina *Zh. Russ. Fiz.-Khim. O-va.* **1918**, *50*, 553–557.
(20) (a) M. Gomberg *Ber. Dtsch. Chem. Ges.* **1900**, *33*, 3150–3163. (b) M. Gomberg *J. Am. Chem. Soc.* **1900**, *22*, 757–771. (c) H. Lankamp, W. T. Nauta, C. MacLean *Tetrahedron Lett.* **1968**, *9*, 249–254.
(21) (a) A. Ye. Chichibabin *Zh. Russ. Fiz.-Khim. O-va.* **1902**, *34*, 137–140. (b) A. Ye. Chichibabin *Zh. Russ. Fiz.-Khim. O-va.* **1901**, *33*, 959–961.
(22) (a) A. E. Tschitscibabin *Ber. Dtsch. Chem. Ges.* **1904**, *37*, 4709–4715. (b) A. Ye. Chichibabin *Zh. Russ. Fiz.-Khim. O-va.* **1908**, *40*, 1367–1376.
(23) A. Ye. Chichibabin *Issledovaniya po voprosu o trekhatomnom uglerode i o stroyenii prosteyshikh okrashennykh proizvodnykh trifenilmetana [Studies on the question of triatomic carbon and the structure of the simplest colored derivatives of triphenylmethane], Dr. Khim. Dissertation*; Tip. Imp. Mosk. un-ta.: Russia, **1912**.
(24) A. E. Tschitschibabin *Ber. Dtsch. Chem. Ges.* **1907**, *40*, 1810–1819.
(25) (a) L. K. Montgomery, J. C. Huffman, E. A. Jurczak, M. P. Grendze *J. Am. Chem. Soc.* **1986**, *108*, 6004–6011. (b) Review: T. T. Tidwell *Adv. Phys. Org. Chem.* **2001**, *36*, 1–58.
(26) (a) A. E. Tschitschibabin *Ber. Dtsch. Chem. Ges.* **1904**, *37*, 186–188. (b) A. E. Tschitschibabin *Ber. Dtsch. Chem. Ges.* **1904**, *37*, 850–853. (c) F. Bodroux *C. R. Hebd. Seances Acad. Sci.* **1904**, *138*, 92–94.