

Wilhelm Schlenk: The Man Behind the Flask**

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In 1943 there appeared in *Berichte der Deutschen Chemischen Gesellschaft*^[1] a brief notice (Figure 1) of the death of Wilhelm Schlenk, the former President of the German Chemical Society (Deutsche Chemische Gesellschaft).^[2a] It was stated that a fuller biography of Schlenk would appear later, but this has not been forthcoming, although there were short articles in specialized Austrian^[2b] and Bavarian^[2c] journals. Underneath the notice about Schlenk there was a list of individuals who had died in 1942, and this list was headed by the traditional German Iron Cross, emblazoned with the swastika, the emblem of the ruling National Socialist Party led by Adolf Hitler. A name that stands out on this list is that of Max Bodenstein, another pioneer in free radical chemistry and one of Schlenk's successors as President of the Deutsche Chemische Gesellschaft (1930–1932), for whom a detailed memorial appeared in 1967.^[2d]

The name Schlenk is familiar to many chemists because of the widespread use of "Schlenk" glassware, as illustrated in many textbooks and reviews on the handling of air-sensitive compounds.^[3] Who was Schlenk, and why has the promised obituary never appeared? A brief study of the life of this extraordinary scientist provides an answer to the first question, and also makes a strong case that he should be better known, not only for his scientific achievements but also for the example he set as a man of principle and political courage.

Wilhelm Johann Schlenk (Figure 2) was born in Munich in 1879, the son of Georg and Emilie Schlenk, and attended the Realgymnasium there. He had a fine singing voice and considered a career in music, but instead followed the example of his brother Johann Oskar Schlenk (1874–1951; Figure 2, right) in the study of chemistry. Another brother Hermann became a Director of the Löwenbräu brewery in

Sitzung am 22. Mai 1943

Vorsitzender: R. Kuhn, Präsident.

Am 28. April 1943 verstarb in Tübingen im Alter von 64 Jahren der frühere Präsident der Gesellschaft Hofrat Professor Dr.

WILHELM SCHLENK.

In einem Nachruf in den „Berichten“ wird seiner besonders gedacht werden.

Die Gesellschaft verlor am 13. Mai 1943 eines ihrer ältesten Mitglieder; in Brünn verstarb der seit 1886 der Deutschen Chemischen Gesellschaft angehörende Professor Dr. h. c.

GUSTAV ULRICH.

Die Anwesenden ehren das Andenken an die Toten durch Erheben von den Sitzen.

Herr Dipl.-Ing. Horst Ademeit (Potsdam) erhielt als Leutnant der Luftwaffe das Ritterkreuz zum Eisernen Kreuz. Die Gesellschaft sprach ihrem Mitglied die besten Glückwünsche zu der hohen Auszeichnung aus.

In der Sitzung wurde folgender Vortrag gehalten:

K. Freudenberg (Heidelberg): Beiträge zur Chemie der Kohlenhydrate.

Der Vorsitzende:

R. Kuhn.

Der Schriftführer:

R. Weidenhagen.

Mitteilungen der Gesellschaft.

Die Toten aus dem Jahre 1942



Für Großdeutschland sind gefallen:

Benecke, Dr. Hans Joachim, Stöckheim/Altmark Krs. Salzwedel,
John, Dr. phil. habil. Walter, Göttingen,
Junge, Dipl.-Ing. Werner, Berlin,
Schlötzer, Dr. Arnulf, Berlin,
Will, Dr.-Ing. Erich, Berlin.

Es sind verstorben:

Antrick, Dir. Dr. Otto, Berlin; Becka, Prof. Dr. Jan, Brünn; Betti,
Prof. Dr. Mario, Bologna (Italien); Bodenstein, Prof. Dr. Max, Berlin;
Brüggemann, Dir. Dr. R., Singen; Claasz, Prof. Dr. M., München; Da-
rapsky, Prof. Dr. A., Köln a. Rh.; Degen, Dr. Jos., Düren/Rhld.; Ehrlich,

Figure 1. Announcement of the death of Wilhelm Schlenk in *Berichte der Deutschen Chemischen Gesellschaft*, 1943.

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Munich. Oskar was a student of Adolf von Baeyer and Johannes Thiele in Munich and after a brief stay at the University in Heidelberg in 1900 spent his career at the Heyden chemical company in Radebeul near Dresden. He worked on pharmaceuticals, and published papers on the 100th anniversaries of the discoveries of benzene by Faraday and of aniline by Unverdorben, and a historical paper on aspirin. Wilhelm also studied in the Chemistry Department of the Academy of Science in Munich, which was led by the

compound that was almost completely dissociated in solution (Figure 4). This paper also reported that triphenylmethyl cation was reduced to the triphenylmethyl radical [Eq. (1)], removing all doubt as to the existence of the radical. This ended the first phase of the study of triarylmethyl radicals, which had consumed a decade to reach agreement on the correctness of Gomberg's original claims.

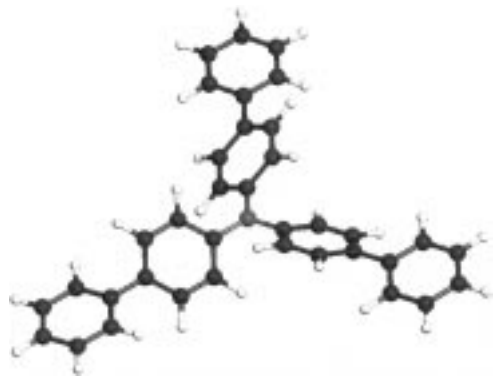


Figure 4. Structure of the tris(4-biphenyl)methyl radical **2c** (courtesy of Huda Henry-Riyad).

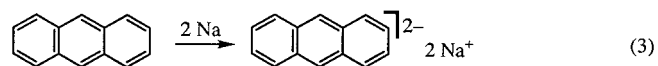
At the same time Schlenk also proposed the radical structure of the ketyl radical anion **3** of benzophenone,^[7b] first prepared by Beckmann and Paul [Eq. (2)].^[7c] This was a



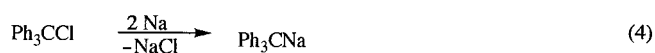
new type of radical and has become well known in chemistry laboratories around the world for its utility as an indicator for the dryness of solvents, as the characteristic blue color of the ketyl in the distilling flask is quenched by the presence of moisture.

These discoveries established Schlenk's reputation as a young chemist of great promise and he moved in 1913 to an extraordinary (Associate) Professorship at the University of Jena. This department was established as a leading research center by the presence of Ludwig Knorr, who served as President of the Deutsche Chemische Gesellschaft from 1915–1916. Another prominent chemist there was Ludwig Wolff, who was responsible for two name reactions, not only the Wolff rearrangement of diazo ketones to ketenes, but also the Wolff–Kishner reduction.

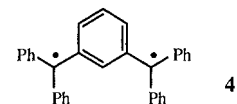
In Jena Schlenk continued to study ketyls,^[7d] and in 1914 also reported the formation of alkali metal addition compounds of alkenes, such as stilbene, and of aromatic hydrocarbons, as in the reaction of anthracene with sodium to produce disodium anthracene [Eq. (3)].^[7e] The reaction of triphenylmethyl radical with sodium gave Ph_3CNa ,^[7f] which



was also obtained from the reaction of Ph_3CCl with sodium [Eq. (4)].^[7g] He and Brauns^[7h,i] reported in 1915 the first



stable diradical, the Schlenk hydrocarbon (**4**). In 1917 Schlenk and Holtz^[7j] reported the preparation of the sodium compounds RNa ($\text{R} = \text{Me}, \text{Et}, n\text{Pr}, n\text{Oc}, \text{Ph}, \text{and Bn}$) and also the first organolithium compounds $\text{MeLi}, \text{EtLi}, \text{and PhLi}$ by exchange reactions from the mercury derivatives forming lithium amalgam [Eq. (5)].

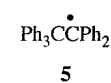


Schlenk gave vivid descriptions of the properties of these compounds, methyl lithium was said to burn in air forming a brilliant red flame with a shower of golden sparks.



This stunning series of successes was enough to gain Schlenk the call to Vienna as ordinary Professor and Director of the Chemical Institute II in 1918, and also a nomination for the Nobel Prize. As described by Ebersson^[8] this nomination received serious consideration, and Schlenk was granted more credit than Gomberg for the final proof of the triarylmethyl radical structure. His synthesis of organolithium compounds was also noted, but it was felt that such compounds were too unstable to be of much use. Ultimately this nomination foundered on the grounds that the prize could not be given to Schlenk alone without Gomberg, but as Gomberg had not been nominated that year he was not eligible for consideration. This ultimately proved fatal to the chances of both men, for when both were nominated for the prize in 1924 Gomberg's work was no longer considered recent enough to qualify, and Schlenk alone did not deserve full credit for the discovery.^[8]

In Vienna Schlenk continued his studies related to triarylmethyl radicals, and with his student Hermann Mark reported the preparation of the pentaphenylethyl radical (**5**).^[9a] Mark later followed Schlenk to Berlin and joined Fritz Haber at the Kaiser Wilhelm Institute, and had an extraordinary career in industry in Germany, and then as Professor in Vienna before going into industry in Canada, and finally became the leader in the development of the polymer program at the Brooklyn Polytechnic Institute (now Polytechnic University).^[9b]



Schlenk had a reputation for his lectures with demonstrations and on 15 January, 1921, he made a presentation at the gala opening of the new "Hörsaal" for the Chemical Institute II at the Vienna University before a large audience that included Albert Einstein (Figure 5). The title of the lecture was "Applications of Electricity in Chemistry",^[10a] as related by his son Hermann he had obtained a new electrical apparatus but ignored warnings not to use this for the actual demonstration and received a tremendous electrical dis-

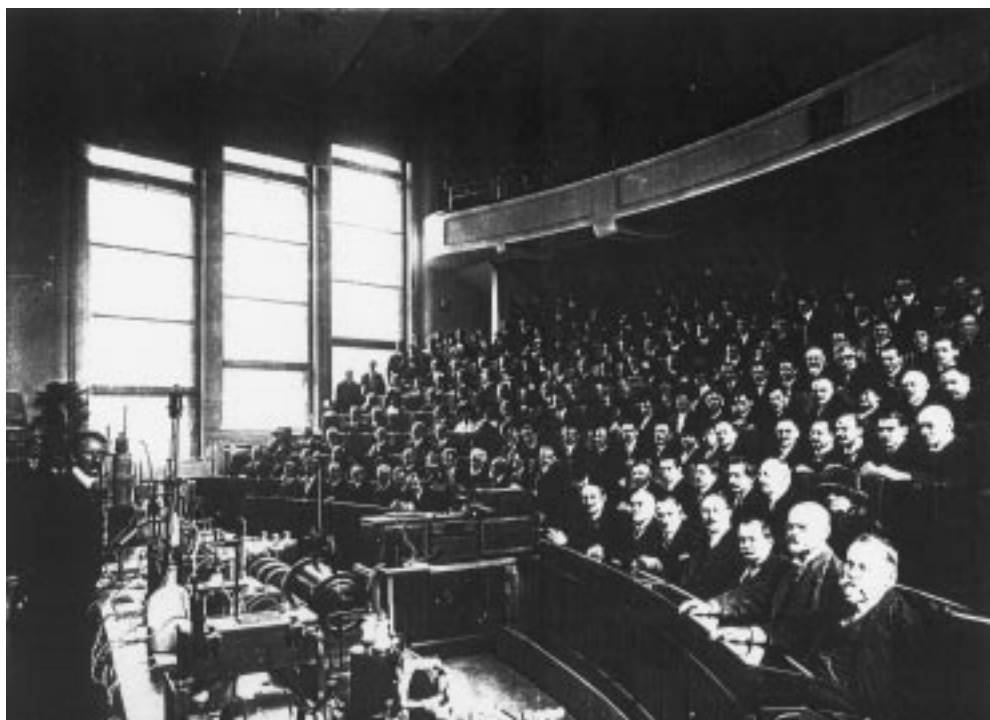


Figure 5. Schlenk at the dedication of the new lecture hall in Vienna, January 15, 1921. Albert Einstein is in the second row, third from right. Schlenk's sons Wilhelm and Fritz are in the balcony. This hall was renovated and rededicated, May, 2000. (Photo courtesy of Edward Schlenk)

charge, which could be seen going in one finger and out the other hand. Schlenk was thrown to the floor, but revived and finished the lecture.

With the death of Emil Fischer in 1919 the Chair at the Friedrich Wilhelms (now Humboldt) University in Berlin became vacant. This was the most prestigious chair in Germany, Richard Willstätter, the first choice for the position, declined to leave Munich.^[10c] Fritz Haber was also considered as a successor, but the influential industrialist Carl Duisberg argued strenuously that an organic chemist should occupy the position, as this was vital to the interests of German industry. The German economy was heavily dependent upon the manufacture of organic chemicals, and was suffering from the ravages of the war and the large reparations which had been imposed afterwards. In 1921 the Chair was offered to Schlenk, who became Director of the Chemical Laboratory. Haber was Professor at the Kaiser Wilhelm Institute at Dahlem, a suburb of Berlin, and a friend of Schlenk's, but was also immensely ambitious, and was given a Chair of Industrial Chemistry at the University. In Berlin the Schlenk family lived in quarters attached to the Chemical Laboratory on Hessische Strasse (Figure 6), erected in 1900 for Emil Fischer. Schlenk's three sons would visit the laboratory,^[10b] which evidently stimulated their interest in chemistry, as all three (Figure 7) became successful chemists: Wilhelm, Jr. (1907–1975, Ph.D. 1929, Technical University of Berlin, with Robert Pschorr), Fritz (1909–1998, Ph.D. 1934, Berlin, with Wilhelm Schlenk, Sr.), and Hermann (born 1914, Ph.D. 1939, Munich, with Heinrich Wieland).

In the aftermath of the First World War Germany was largely excluded from international scientific activities by the victorious allies. However in June, 1921, there was a meeting in Utrecht in the Netherlands, which had been neutral in the

war, to plan for an international conference, and Schlenk along with Paul Walden from Germany and Rudolph Wegscheider from Austria participated in the organizational meeting. This conference, the *Réunion Internationale de Chimie* was duly held in Utrecht June 21–23, 1922, with extensive participation from Europe and the United States, and the lecturers included Schlenk,^[10d] Paul Walden, and Heinrich Wieland from Germany, and William Albert Noyes from the U.S.A.

Also in 1922 Schlenk became a Vice President of the Deutsche Chemische Gesellschaft, the German Chemical Society, and was President from 1926–1928. Increasingly he was involved in administration and in international science, and in 1927 he attended the centennial jubilee of the birth of Berthelot in Paris, along with Willstätter, Wieland, Haber, and Walther Nernst.^[10e,f] Not since the war had German chemists been invited to such an event in France. Then in 1928 Schlenk along with Haber and Alfred Stock attended the International Congress of Pure and Applied Chemistry (IUPAC) in the Hague.^[10e] As the German Chemical Society was still not a member of (IUPAC) at that time, they came not with official but with personal invitations. However in 1930 at the 10th IUPAC Conference in Liège Schlenk was part of an official German delegation. In 1931 he was a lecturer at the Solvay Conference on Chemistry in Brussels, along with Robert Robinson and Christopher K. Ingold from Britain, and Hermann Staudinger from Germany.^[10g]

In 1924 Schlenk authored a chapter on organometallic chemistry in *Die Methoden der Organischen Chemie*^[3a] describing the techniques of handling sensitive materials in glass apparatus, and these techniques were incorporated in many later books and reviews.^[3] Some of his innovative designs are illustrated in Figure 8, and it is for this apparatus

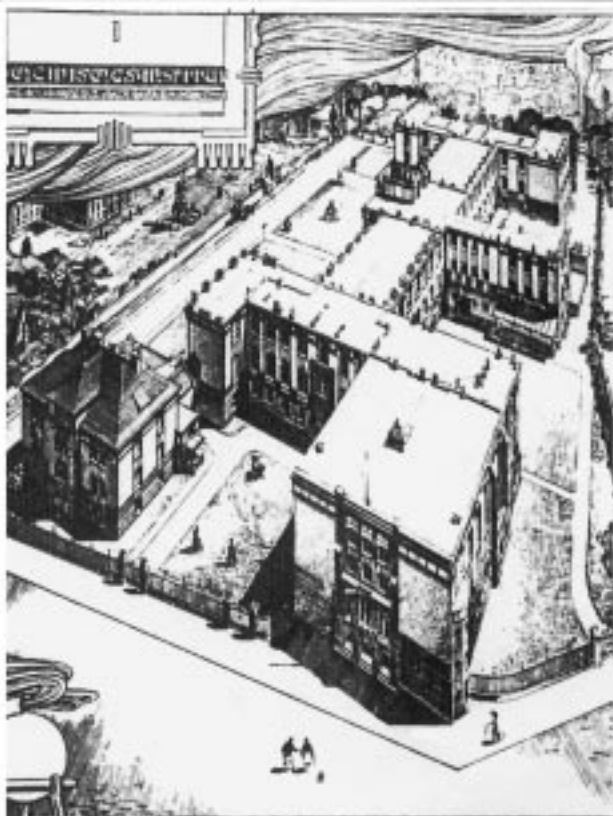


Figure 6. Top: Director's house. Note passageway to private laboratory in Institute (Photo by Wilhelm Schlenk). Bottom: the chemical laboratory on Hessische Strasse in Berlin, for which there was a centennial celebration in June, 2000. The Director's house is on the left corner.



Figure 7. Schlenk's children: Wilhelm, Hermann, Fritz, with Wilhelm, Sr., and Mathilde, about 1922 (courtesy of Gertrude Lenzer).

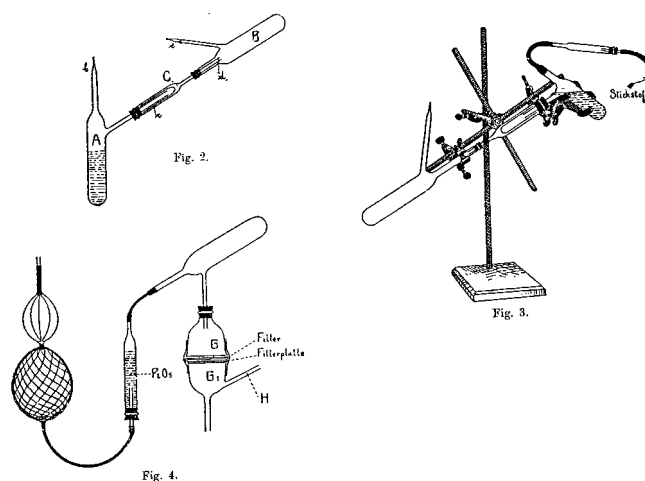
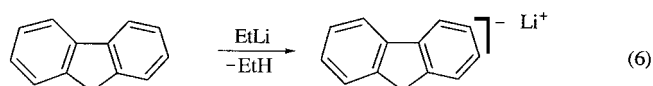


Figure 8. Schlenk glassware (from reference [7d]).

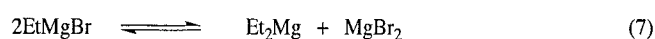
Schlenk's name is most widely known. The pivoting device for transfers was known as a "Schlenk Kreuz", or Schlenk cross.^[3e]

From 1921–1925 Ernst Bergmann was a doctoral student with Schlenk, and remained in Berlin as a Privatdozent from 1928. Together with a sizeable group of students Schlenk and Bergmann engaged in comprehensive studies of the reactions of aromatic alkenes with alkali metals. One important result of this work was the discovery of the direct lithiation of hydrocarbons by organolithiums, as in the reaction of fluorene

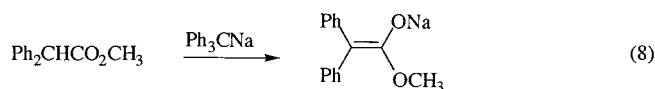
with ethyllithium [Eq. (6)].^[11a] With his son Wilhelm, Jr., Schlenk proposed the equilibrium of Grignard reagents with



diethylmagnesium, known thereafter as the "Schlenk equilibrium" [Eq. (7)].^[11b] Another major discovery was the



preparation and study of crystalline enolates [Eq. (8)].^[11c] Eugen Müller (1905–1976)^[11d] was one of Schlenk's students at this time, and later as Professor at Heidelberg and Tübingen became well known for his own research on free radicals.



There was competition with Karl Ziegler at Heidelberg on the reactions of alkali metals with allenes. Ziegler was a younger man rising to prominence who made important contributions in free radical chemistry of the Gomberg type as well as in organometallic chemistry. Later this was to lead to the discovery of the polymerization of olefins by organometallic compounds, for which Ziegler was awarded the Nobel Prize in 1963.

Schlenk published with Bergmann in 1932 the first volume, of 805 pages, of a comprehensive textbook on organic chemistry.^[12a] In his last scientific paper Schlenk was a coauthor with Bergmann of a paper regarding the structure of steroid derivatives.^[12b] At this stage Bergmann was pursuing research independently, but he left Germany in 1933 and achieved great prominence not only as the founder of organic chemistry in Israel but also as a scientific advisor to the government.^[12c,d]

With the ascension to power of the National Socialist Party under Adolf Hitler in January, 1933, the position of Schlenk became tenuous, as he made his democratic ideals known, for example refusing to begin his lectures with the expected "Heil Hitler".^[10b] He offered his position in Berlin to Willstätter when the latter resigned his Chair in Munich in 1925 because of the increasing anti-Jewish sentiment,^[13a] and in 1932 published a 60th birthday tribute to Willstätter.^[13b] He also remained close to Haber, and authored a prominent memorial to Haber on his death in 1934.^[13c] Haber had suggested in 1933 that Schlenk should take his place as Vice-President of IUPAC,^[10f] but this was anathema to the Nazis. With his close association with Jews such as Haber, Willstätter, and Bergmann, and his outspoken convictions Schlenk's influence was finished. He was conspicuously absent from an important international conference on free radicals organized by the Faraday Society in Cambridge in September, 1933, although others from Germany including Ziegler were in attendance, as well as some who were already émigrés, such as Friedrich Paneth and Michael Polanyi.^[13d]

In 1935 Schlenk was removed from his Chair in Berlin and became Professor at Tübingen, where there was a more tolerant atmosphere. There he was a visible symbol of resistance and demonstrated that one could dare to take risks on matters of principle and still survive. The Berlin Chair remained vacant for the next 10 years.

Schlenk remained in Tübingen for the remainder of his career, but was heavily involved in teaching and administration and published no more research papers, not even from the thesis of his son Fritz.

In 1939 the second large volume of his textbook appeared,^[14a] although for reasons of expediency without Bergmann

as coauthor, to his great displeasure, as he had written much of the text.^[12d, 14b] A third volume was reported to be almost complete, but this never appeared. There was some mention of a possible position in Istanbul, but this did not materialize.^[14c] In 1942 he was expelled from the Deutsche Chemische Gesellschaft,^[2c] and suffered ill health before his death in 1943.^[15] His son Wilhelm, Jr., also ended his academic career and went into industry at BASF, and his other sons Fritz and Hermann emigrated to the United States. Fritz was at the University of Illinois in Chicago, and Hermann at the Hormel Institute of the University of Minnesota. All three sons published extensively.

Schlenk was eulogized in a 60th birthday tribute in Tübingen,^[15] and in a notice on his death,^[15] but these were not published. These emphasized his devotion to science and to his students, and describe his unassuming character and quest for scientific truth not personal acclaim or power. He personally devoted long hours to cleaning the glassware from the lecture demonstrations, and after his early morning walks in Tübingen was in the laboratory at 6 am and available for the students. Schlenk was a tall man, characterized as "long Schlenk" in a memoir^[15] and was noted for his devotion to the arts. Wieland's brief testament to Schlenk^[2c] also describes a courageous and humane individual.

Returning to the questions posed earlier the identity of Wilhelm Schlenk is available in the published record, and he was one of the most talented chemists of the first third of the 20th Century. His work was widely recognized early in his career, for example both tris(4-biphenyl)methyl radical **2c**^[7a] and sodium benzophenone ketyl **3**^[7b] played a prominent role in the development by Gilbert N. Lewis of his theory of the electron pair bond.^[16a] One of the Schlenk diradicals was used by Erich Hückel in considering the application of Hund's rule to diradicals.^[16b] The answer to why the promised detailed memorial has never appeared is open to speculation. It is even somewhat surprising that his death was prominently mentioned in 1943^[2a] in view of the animosity of the Nazis.

He has been commemorated in the Arfvedson–Schlenk Prize in Lithium Chemistry of the GDCh sponsored by Chemetall GmbH, which was awarded for the first time in 1999, to Paul von R. Schleyer. If Schlenk had survived the war and continued his career he may have received further honors, as did Wieland and Paneth. His two most prominent students, Mark and Bergmann, had emigrated, and thus his personal history has been largely forgotten, although his work with free radicals and organometallics, and especially his techniques for handling air-sensitive compounds, still remain prominent. Extensions of his work include the determination of the crystal structures of ethyllithium,^[16c] ester enolates,^[16d] and sodium benzophenone ketyl.^[16e] There is great interest in "high spin" molecules inspired by the Schlenk diradical **4**; and continued prominence for the "Schlenk equilibrium",^[16f] which has recently been extended to lanthanide(II) aryls.^[16g]

He also deserves to be remembered as a man of courage and integrity who dared to risk his high position in opposition to tyranny. He is an example to scientists of all countries that the pursuit of knowledge does not preclude the duty to defend moral principles.

- [1] In 1949 the society was reorganized and renamed *Gesellschaft Deutscher Chemiker* (GDCh) and in 1947 the name of the journal was changed from *Berichte der Deutschen Chemischen Gesellschaft* to *Chemische Berichte*.
- [2] a) *Ber. Dtsch. Chem. Ges.* **1943**, 76A, 59; b) E. Späth, *Alm. Akad. Wiss. Wien* **1943**, 93, 208–212; c) H. Wieland, *Bayer. Akad. Wiss. Jahrb.* **1948–1949**, 249–251; d) *Chem. Ber.* **1967**, 100, xcvi–cxxvi.
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- [4] a) O. Piloty, B. G. Schwerin, *Ber. Dtsch. Chem. Ges.* **1901**, 34, 1863–1870; O. Piloty, B. G. Schwerin, *Ber. Dtsch. Chem. Ges.* **1901**, 34, 1870–1887; O. Piloty, B. G. Schwerin, *Ber. Dtsch. Chem. Ges.* **1901**, 34, 2354–2367; b) A. R. Forrester, J. M. Hay, R. H. Thompson, *Organic Chemistry of Stable Free Radicals*, Academic Press, London, **1968**; c) C. Harries, *Ber. Dtsch. Chem. Ges.* **1920**, 53A, 153–168.
- [5] W. Schlenk, U.S. Patent 895,689, **1908** [*Chem. Abstr.* **1908**, 2, 3286].
- [6] a) M. Gomberg, *Ber. Dtsch. Chem. Ges.* **1900**, 33, 3150–3163; M. Gomberg, *J. Am. Chem. Soc.* **1900**, 22, 757–771; b) J. M. McBride, *Tetrahedron* **1974**, 30, 2009–2022; c) for descriptions of the further development of free radical chemistry see C. Rüchardt, *Sitzungsber. Heidelb. Akad. Wiss. Math. Naturwiss. Kl.* **1992**, 319–345, and T. T. Tidwell, *The Chemical Intelligencer* **2000**, 6(3), 33–38.
- [7] a) W. Schlenk, T. Weickel, A. Herzenstein, *Justus Liebigs Ann. Chem.* **1910**, 372, 1–20; b) W. Schlenk, T. Weickel, *Ber. Dtsch. Chem. Ges.* **1911**, 44, 1182–1189; c) E. Beckmann, T. Paul, *Justus Liebigs Ann. Chem.* **1891**, 266, 1–28; d) W. Schlenk, A. Thal, *Ber. Dtsch. Chem. Ges.* **1913**, 46, 2840–2854; e) W. Schlenk, J. Appenrodt, A. Michael, A. Thal, *Ber. Dtsch. Chem. Ges.* **1914**, 47, 473–490; f) W. Schlenk, E. Marcus, *Ber. Dtsch. Chem. Ges.* **1914**, 47, 1664–1687; g) W. Schlenk, R. Ochs, *Ber. Dtsch. Chem. Ges.* **1916**, 49, 608–614; h) W. Schlenk, M. Brauns, *Ber. Dtsch. Chem. Ges.* **1915**, 48, 661–669; i) W. Schlenk, M. Brauns, *Ber. Dtsch. Chem. Ges.* **1915**, 48, 716–728; j) W. Schlenk, J. Holtz, *Ber. Dtsch. Chem. Ges.* **1917**, 50, 262–274.
- [8] L. Ebersson, *The Chemical Intelligencer* **2000**, 6(3), 44–49.
- [9] a) W. Schlenk, H. Mark, *Ber. Dtsch. Chem. Ges.* **1922**, 55, 2285–2299; b) H. Mark, *From Small Organic Molecules to Large. A Century of Progress*, ACS, Washington, **1993**.
- [10] a) *Österr. Chem. Ztg.* **1921**, 22, 18; b) Cornelia Schlenk and Edward Schlenk, private communications; c) W. Ruske, *100 Jahre Deutsche Chemische Gesellschaft*, Verlag Chemie, **1967**; d) W. Schlenk, *Recl. Trav. Chim.* **1922**, 41, 561–564; e) Described in V. N. Ipatieff, *The Life of a Chemist*, Stanford University Press, **1946**; f) D. Stoltzenberg, *Fritz Haber. Chemiker, Nobelpreisträger, Deutscher, Jude*, VCH, Weinheim, **1994**, p. 565, p. 603; g) W. Schlenk, *Inst. Int. Chim. Solvay Cons. Chim.* **1931**, 503–523.
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- [12] a) W. Schlenk, E. Bergmann, *Ausführliches Lehrbuch der Organischen Chemie*, Vol. 1, Deuticke, Leipzig, **1932**; b) W. Schlenk, O. Bergmann, E. Bergmann, *Chem. Ind. Trans.* **1933**, 52, 209–210; c) For an obituary of Bergmann: K. R. S. Ascher, E. Shaaya, *Phytoparasitica* **1975**, 3, 145–147; d) for an essay on Bergmann: D. Ginsberg, *Israel J. Chem.* **1963**, 1, 323–350.
- [13] a) R. Willstätter, *Aus Meinem Leben*, Verlag Chemie, Weinheim, **1973**, p. 347; b) W. Schlenk, *Angew. Chem.* **1932**, 33, 529–531; c) W. Schlenk, *Ber. Dtsch. Chem. Ges.* **1934**, 67A, 20–23; d) *Trans. Faraday Soc.* **1934**, 30, 1–248.
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