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MOSES GOMBERG

1866–1947

The death of Moses Gomberg on February 12, 1947, brought to a close the career of a brilliant scientist who had won recognition as one of the world's leading authorities in organic chemistry. He was born on February 8, 1866, in the small town of Elizabetgrad, Russia, the son of George and Marie Resnikoff Gomberg. From 1878 to 1884 he was a student in the Nicolau Gymnasium of his native town. In the latter year his father was accused of anti-Czarist activities and was forced to flee with his family, and his estate was confiscated. With help from friends they were able to go to Chicago where for a time hardship became their lot. Neither father nor son had a knowledge of English and they both worked in Chicago at whatever occupation they could find, and for a time at least in the stockyards. The son, however, with indomitable energy earned the means to complete his high school course and to enter the University of Michigan from which he was graduated in 1890 with the degree of Bachelor of Science. An assistantship enabled him to continue in graduate work, and two years later he received the degree of Master of Science. He took his doctorate in 1894 with a thesis on the reactions of caffeine, under Professor A. B. Prescott.

Even before his appointment as instructor in 1893, he was planning to study abroad and in order to earn the necessary funds, he spent his spare time in analyzing materials for his numerous clients. His versatility is shown by the fact that his work included the analysis of minerals, water, fats and oils, foods, patent medicines and drugs. He was also employed frequently as an expert witness in toxicology cases, and he thoroughly enjoyed matching wits with the opposing lawyers. However, he was greatly disturbed by the necessity of doing this type of work because it interfered with the progress of his research, and he dropped it as soon as possible. Thereafter he refused steadfastly to accept consulting work of any kind.

A leave of absence in 1896–1897 permitted a year of study in Germany and he decided to spend two terms in Baeyer's laboratory in Munich. Thiele suggested a problem involving the preparation of isonitramino- and nitroso-isobutyric acid, and this work resulted in a 22-page paper in Liebig's *Annalen.*

The third term of the year was spent in Victor Meyer's laboratory in Heidelberg. In discussing the choice of a problem, Gomberg said that he wanted to prepare tetraphenylmethane. Meyer, as well as other chemists, had been interested in the synthesis of this compound and had tried various methods but without success. Consequently, Meyer suggested other more suitable problems but Gomberg was determined to go ahead, and his confidence was well deserved for he was successful in his attempt. His method consisted in oxidizing triphenylmethanehydrazobenzene to the corresponding azo-compound and heating the latter to 110–120°. However, the yield was very poor, only 2–5%.

His next step, when he returned to the University of Michigan, was to investigate the preparation of the related hexaphenylethane in the hope of obtaining this completely phenylated hydrocarbon in greater yield. Accordingly, triphenylchloromethane in benzene was treated with sodium but without appreciable action. However, when molecular silver was used, a colorless compound precipitated, which was assumed to be hexaphenylethane. An elementary analysis gave low values for the percentage of both carbon and hydrogen. When further analyses gave the same result, it was concluded that the compound contained oxygen; and, after the silver had been shown to be free of oxide, it was suspected that oxygen of the air was oxidizing the initially formed hydrocarbon. By working in the absence of air, Gomberg obtained a hydrocarbon which was extremely unsaturated in its behavior. In benzene solution it absorbed chlorine, bromine and iodine, and when exposed to air a stable peroxide was formed. In view of these remarkable properties, in his first paper (1900) on the hydrocarbon, Gomberg wrote, "The experimental evidence . . . forces me to the conclusion that we have to deal here with a free radical, triphenylmethyl, $(C_6H_5)_3C$. On this assumption alone do the results described above become intelligible and receive an adequate explanation." Following the publication of this paper, other chemists[1] immediately became interested in his hydrocarbon, and confirmed its striking properties. Moreover, it was shown that triphenylmethyl was but one of a large group of similar triarylmethyls.

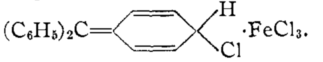
However, for almost ten years, the existence of free radicals was questioned. Although the chemical evidence in favor of the trivalency of carbon was convincing, molecular weight determinations of the hydrocarbon indicated a value practically double that of the free radical. Consequently, a great deal of skepticism was shown, for there had been other somewhat similar cases involving radicals such as Gay Lussac's cyanogen, Bunsen's cacodyl, and Frankland's and also Kolbe's alkyls. These had been described as free radicals but later were found to be dimolecular; and it was assumed that Gomberg's hydrocarbon was just another instance of history repeating itself; and the concept of free radicals was ignored.

The situation in the period of 1900–1905 was confused by the fact that the new hydrocarbon was not regarded as hexaphenylethane because its properties were so different from what were expected. Furthermore, in 1902 Ullmann and Borsum had prepared a compound which was universally accepted as hexaphenylethane until Chichibabin showed two years later that it was *p*-benzohydryltetraphenylmethane

In the meantime, various quinonoid structures had been suggested, but none of them proved satisfactory in explaining the unique properties of the Gomberg hydrocarbon. As all attempts to prepare a different hydrocarbon with the structure of hexaphenylethane failed, the majority of chemists began to look upon Gomberg's compound as hexaphenylethane, and considered it to be unstable (*i. e.* reactive to iodine, oxygen, etc.) *per se*. Gomberg, however, remained unshaken in his belief in the existence of triphenylmethyl and time and again reiterated his faith in the concept of free radicals.

A study of other triarylmethyls hastened considerably the acceptance of the idea of free radicals, and an early suggestion (Flürscheim, 1905) that colorless hexaphenylethane dissociates in solution into colored free radicals, $Ar_3C—CAr_3 \leftrightarrows 2Ar_3C$, was adopted. Under comparable conditions some radicals, like triphenylmethyl, remain only slightly unassociated, others are present in solution to a greater extent (20–80%), while others, like tri-*p*-biphenylmethyl (Schlenk) exist as free radicals even in the solid state.

Later, Wieland showed that tetraphenylhydrazine dissociates to give a free radical with divalent nitrogen, and other cases of free radicals with abnormal valences were reported. It was evident that Gomberg had opened an entirely new field in chemistry which was of extreme importance. This was further emphasized when Paneth demonstrated the transitory existence of the radicals ethyl and methyl, and it was soon shown that such transitory radicals are intermediate products in certain chemical reactions.

Another phase of Gomberg's work was concerned with the development of the quinonoid theory. Solutions of triphenylmethyl have an orange-yellow color, and Schmidlin found that there is both a colorless and a colored form present. In order to account for the two forms, Gomberg assumed that one of them must be quinonoid. In 1901, Gomberg and other investigators obtained double salts of triphenylchloromethane which were intensely colored, and Kehrmann assigned a quinonoid structure to such compounds, *e. g.*,  $(C_6H_5)_2C{=}C_6H_4{<}^{H}_{Cl}\cdot FeCl_3$. Baeyer vigorously opposed this view and claimed that the color was due to salt formation, and could be explained on the basis of his theory of halochromism. In considering this problem, Gomberg reasoned that if there was a quinonoid form of *p,p′,p″*-tribromotriphenylchloromethane in solution in liquid sulfur dioxide, a bromine atom would become labile and a shift of chlorine and bromine might

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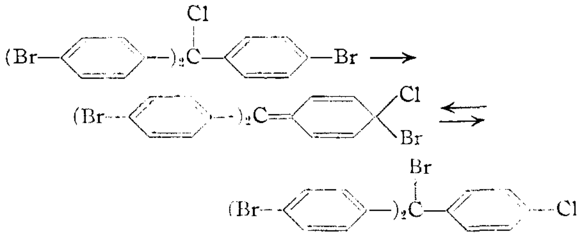
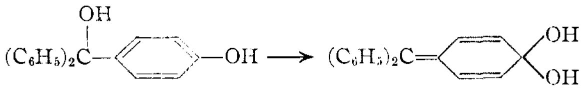
[1] Among the chemists who participated in the discussion of the structure of the unusual hydrocarbon were Baeyer, Markownikoff, Thiele, Flürscheim, Schmidlin, Werner, Hantzsch, and Wieland.

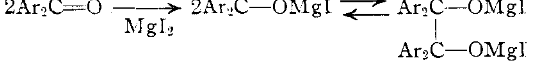
be expected. To test this idea, he dissolved *p,p',p''*-tribromotriphenylchloromethane in liquid sulfur dioxide, and, after a few days allowed the sulfur dioxide to evaporate slowly. The resulting product contained 85% of *p,p'*-dibromo-*p''*-chlorotriphenylbromomethane.



The shift of the chlorine atom and the bromine atom provided positive evidence in favor of the quinonoid theory. But in no case so far, had it been possible to isolate the two tautomeric forms of any triarylmethyl salt. However, Gomberg was able to isolate the benzenoid and the quinonoid form of *p*-hydroxytriphenylcarbinol in the crystalline state, thus helping to establish the quinonoid theory on a firm basis.

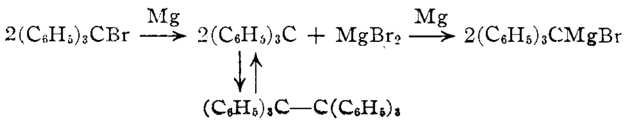


One of his last investigations was concerned with a study of the reducing action of the binary system $Mg + MgI_2$ on organic compounds in anhydrous ether and benzene. Gomberg postulated that the active reducing agent was magnesious iodide which was formed by interaction of the metal and its halide according to the following formulation: $Mg + MgI_2 \rightleftarrows 2MgI$. This hypothesis served to explain the reduction of $C{=}O$, $C{=}N$, $N{=}N$, and other unsaturated groups in compounds. By this new reducing agent aromatic ketones were reduced to pinacols in high yields through the intermediate formation of colored free radicals (analogs of sodium ketyls).



$$2Ar_2C{=}O \xrightarrow[MgI_2]{Mg} 2Ar_2C{-}OMgI \rightleftarrows \begin{array}{l} Ar_2C{-}OMgI \\ \;| \\ Ar_2C{-}OMgI \end{array}$$

Aromatic aldehydes, acids and their alkyl esters were found to be converted into benzoins. In the preparation of the Grignard reagent from triphenylmethyl bromide and magnesium Gomberg showed that the first step is the quantitative formation of triphenylmethyl ⇄ hexaphenylethane. The Grignard reagent is produced in the second step by the reaction of the free radical with the mixture of magnesium and magnesium bromide.



$$2(C_6H_5)_3CBr \xrightarrow{Mg} \begin{array}{c} 2(C_6H_5)_3C \\ \downarrow\uparrow \\ (C_6H_5)_3C{-}C(C_6H_5)_3 \end{array} + MgBr_2 \xrightarrow{Mg} 2(C_6H_5)_3CMgBr$$

The reaction is unique in that a Grignard reagent can be prepared from a hydrocarbon (hexaphenylethane).

Other investigations included the first synthesis of unsymmetrical tetraphenylethane and one of the first syntheses of pentaphenylethane, the preparation of benzyl ethers of carbohydrates, the synthesis and study of certain dyes, a study of the $(ClO_4)_x$ radical, and the synthesis of biaryls by the diazo reaction (Gomberg reaction). However, an examination of his publications reveals that most of his life was devoted to the investigation of triarylmethyls and related compounds.

Professor Gomberg was a member of many learned societies: the American Philosophical Society; A Fellow of the American Association for the Advancement of Science; the Franklin Institute; the National Academy of Sciences; the American Institute of Chemists; the Netherlands Chemical Society, of which he was an honorary member; and the American Chemical Society, of which he was president in 1931. His achievements were recognized by the award of various honors: he was the recipient of the Nichols Medal in 1914; of the Willard Gibbs Medal in 1925; and of the Chandler Medal in 1927. He received the degree of Doctor of Science from the University of Chicago in 1929, the same degree from the Brooklyn Polytechnic Institute in 1932, and the degree of Doctor of Laws from the University of Michigan in 1937. He would have been less than human had he not been pleased by these marks of distinction, but none of them ever changed the even tenor of his ways. All evidences of his attainments were received with modesty that was one of his characteristic traits. He never sought preferment, and all forms of academic advertising were alien to his soul.

During the first World War he joined the group of civilian chemists working on gas warfare under the direction of the Bureau of Mines, prior to the organization of the Chemical Warfare Service. His assignment was the preparation of mustard gas; and although this was abhorrent to his nature, he accepted it without hesitation. Ethylene chlorohydrin was the intermediate which was required, and the method which he developed was the first in this country for the commercial preparation of this important compound. This work was done in his laboratory in Ann Arbor. Later in 1918, he was commissioned as Major in the Ordnance Department, acting as an advisor in the manufacture of smokeless powder and high explosives. Except for the year of study in Germany, this was the only break in his teaching career which extended over a period of 43 years.

He was chairman of the Department of Chemistry from 1927 to 1936 when he retired. He stressed the necessity of a thorough basic training in all branches of chemistry with a minimum of specialization. He believed that teaching on the university level was impossible without research, and in regard to Ph. D. candidates he felt that the emphasis should be placed on the training of the candidate and not on the issuance of a publication. He had strong convictions on such matters and was not adverse to expressing them, but he never spoke with harshness or with intent to hurt. In his contacts with students, he was sympathetic, gave generously of his time, and was always ready to offer friendly advice.

Gifted with a remarkable memory, he presented his lectures with the full use of a wealth of historical material and so vividly that they left an indelible imprint on his students. A great teacher and scholar, he inspired his students by his methods and ideals, and his colleagues by the vigor and clarity of his mind. To this greatness, he added an innate kindliness and unassuming modesty that endeared him to all.

He never married and lived quietly and happily with his younger sister.

He was a great scientist, a wise counselor, and a loyal friend whose memory will long remain a living force.

C. S. Schoepfle
W. E. Bachmann

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