Journal of Organometallic Chemistry, 338 (1988) 281–287
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Henry Gilman (1893–1986)

An Appreciation

John J. Eisch

Department of Chemistry, State University of New York at Binghamton, Binghamton, NY 13901 (U.S.A.)

(Received September 8th, 1987)

What ultimately attracts a person to a life in chemistry is the mystery of change. Chemical reactions present our senses with evidence of things in flux: colors in transit, heat evolving, odors emanating; for the adventurous, tastes sampled; and for the unprepared, solutions erupting. Even the very word, "chemistry", acknowledges that changes in composition form the essence of this science, for the term derives from the ancient Arabic word, *al-kimiya*, meaning "the art of transformation". Indeed, the modern Japanese word for chemistry, *kagaku*, is literally the "study of change". Thus, a chemical reaction is a compressed metaphor of all earthly existence, personal and planetary, whose status is truly just a matter of time.

Lest we forget this unavoidable fact of existence, life continues to remind us of our transitory situation. On November 7, 1986, a legendary master of chemical

0022-328X/88/$03.50

change, Henry Gilman, finally passed beyond all change in his 94th year. His colleagues and his students, who had viewed him as a phenomenon, had long marveled at his vitality and productivity: more than one thousand scientific publications over a span of 60 years. They will continue to marvel over the memory of Henry Gilman as their life-enhancing mentor.

There are persons gifted from birth, such as Socrates, who through their vitality, enthusiasm, curiosity and vision act as stimuli on their associates and thereby generate excitement and an enhanced sense of life. In the chemical laboratory Henry Gilman was such a Socrates and from this stemmed his extraordinary success as a teacher and research director. In his students' minds will always remain the image of an impeccably clad, tall figure strolling into a laboratory and in a courteous Bostonian tone inquiring, "What's new?" Then he would stand with his left arm across his chest supporting his upright right forearm, whose hand cupped his jutting chin. With an air of great expectancy and rapt attention, he would rivet his attention on the student and listen. A probing Socratic question or critical comment would be interjected periodically to keep the discourse focused. The student became imbued with Henry Gilman's curiosity, enthusiasm and vigor and would strive zealously in the laboratory, so that he might have a worthy answer to Gilman's inevitable question. The prudent student found it advisable to consult the library and to rehearse in his mind possible answers to the queries Gilman might raise. It became of the greatest importance not to disappoint Gilman's high expectations of his research students.

If Gilman's standards of performance were high for his students, he expected no less of himself. He followed the research progress of his students in minute detail and retained it, even when the Gilman group comprised 20 or more doctoral candidates. He did not insulate himself from them through postdoctoral associates, who in many present-day research groups often handle day-to-day research direction. He spent long hours with the chemical literature and maintained a masterly command of contemporary research from throughout the world. Astonishing as this performance is, it pales in the light of one burden Gilman had to bear for 40 years: diminished and dwindling eyesight. In 1947 he suffered retinal detachments that severely impaired and, coupled with glaucoma, ultimately deprived him of his vision. Thus, for over half his professional career he labored under this handicap but did not give up. Unrelenting, he had the chemical literature read to him many hours daily and actually published more than 500 scientific contributions *after* 1947. That surely attests to an indomitable courage and professional commitment far above human expectations.

Henry Gilman spent his entire career in the Midwest, although he was born and educated in Boston. It was there that he acquired his courtly and urbane manner, as well as his accent, and these continued unchanged through a lifetime in Iowa. All his degrees were earned at Harvard University: B.S., *summa cum laude*, 1915; A.M., 1917 and Ph.D., 1918. As an undergraduate he carried out a study of the phenyl esters of oxalic acid that was directed by a young instructor named Roger Adams and the published results constituted Gilman's first scientific paper [1]. His doctoral research, conducted under the renowned Professor Elmer P. Kohler, concerned the preparative aspects of the Reformatsky reaction and was Gilman's first foray into organometallic chemistry [2]. But what was decisively influential on his future research was a *Wanderjahr* in Europe as a Sheldon fellow. Brief periods of study

were spent in Zurich at the Polytechnicum with Hermann Staudinger; at the Sorbonne in Paris where he was stimulated by the importance the Grignard reagent had attained in France; and at Oxford University with William H. Perkin, Jr. This advanced study helped him to find his scholarly métier. Although his subsequent studies of Grignard additions to ketenes [3], isocyanates and isothiocyanates [4] are echoes of his stay in Staudinger's laboratory, it was his contact with the Grignard reagent that was to fix the main theme of his research for the first 15 years of his academic career [5].

Roger Adams left Harvard in 1919 to assume the headship of the Chemistry Department at the University of Illinois. With an eye for talent that would eventually bring his department to the forefront of organic chemistry, Adams invited Gilman to accompany him to Illinois as an instructor. Gilman accepted, but Adams was not alone in his appreciation of Gilman's promise. Within a year, Iowa State College urged Gilman to join them as an assistant professor and to help build up the chemistry program. As in whatever unleashed his enthusiasm, Gilman's performance at Iowa State outstripped all expectations and by 1923 he was promoted to full professor. He began as he meant to continue and for 55 years he taught and carried out research with phenomenal vigor and success. His name became synonymous with chemistry at Iowa State and in 1974, in recognition of this, the chemistry building was renamed Gilman Hall.

His research laboratory became the American hearth of the Grignard reaction and he its proponent. In detailed studies, the preparative possibilities and limitations, the relative reactivities of various functional groups towards the carbon–magnesium bond, the reaction mechanisms, and the quantitative estimation of Grignard reagents were elucidated in an authoritative fashion. This corpus of over 125 publications on Grignard reagents still stands as an instructive example of how an experimental chemist determines the nature of a chemical reaction [6]. Gilman himself followed his own paradigm as he successively expanded his investigations to encompass organometallics of lead, lithium, tin, silicon and, in some degree, most other main group organometallics. Much of the basic preparation and characterization of what are now designated as σ-bonded organometallic compounds was either pioneered or greatly extended by Gilman and his students. Present research workers who routinely employ organometallic reagents would be amazed to learn how many reagents are traceable to a seminal paper by Henry Gilman. When organometallic chemistry rose to industrial prominence in the early 1950's, polymer chemists found that much of the necessary information concerning compounds of lithium, magnesium, aluminum, silicon and copper had already been gathered and awaited them in Gilman's publications.

The audience at a Gilman lecture or the readers of his publications always found a clear, pleasing style of presentation and a careful marshaling of experimental facts, which was devoid of ungrounded speculation. He realized instinctively that such speculation was the less important, more ephemeral part of any scientific communication. He took genuine pleasure in reporting new findings but at the same time, he explicitly recognized and generously praised the prior work of his colleagues. His papers remained free of polemic or derogation of others' work. When called upon by his results to differ from a published statement, he did so with mildness and courtesy. Such tact stemmed not from mere good manners, but from his deep respect for others.

Gilman's respect for his colleagues and his students manifested itself in many ways. His concern for the personal welfare and future plans of his more than 140 doctoral, 50 masters and 50 postdoctoral co-workers was evident in daily conversations during their time at Iowa State and was maintained through frequent correspondence after they set out into the world. Help with stipends, job placement, change in positions and professional contacts was Gilman's way of fostering the careers of his research students. Ever ready to hear a student's opinion or to engage in discussions ranging far from chemistry, he never tried to dominate any discussion, nor did he engage in negative comment about others. When he had to reprove a student for a misstatement or for failing to carry out some expected experiment, he evinced a quiet dismay punctuated by a drawn-out "Oh". Usually Gilman's boundless curiosity and keen chemical zeal served to kindle a similar love of research in his students, but at the same time his ardor could scorch those who were lukewarm. For the latter, Gilman's reproof could be more explicit. Of a student who had not completed the identification of a reaction product because lunchtime had intervened, Gilman asked incredulously, "What, man, have you ice water in your veins?"

His respect for others was also color blind. Dr. Nathaniel Calloway, the first black student to receive the Ph.D. degree in chemistry west of the Mississippi, studied with Henry Gilman. Subsequently, Gilman welcomed many other black students into his laboratory and trained them for leading positions in teaching and research. Far ahead of his time, he served on the board of Trustees of the Carver Foundation and the Tuskegee Institute and was a proponent of equal opportunity for blacks when the issue was unpopular. In the words of Martin Luther King, he judged men by the quality of their minds and the content of their character, rather than by the color of their skin.

His professional activities in editorial work and writing contributed greatly to the growth of organic chemistry in the United States. He served as associate editor of both the Journal of the American Chemical Society and Chemical Reviews. He collaborated with Morris Kharasch in founding the Journal of Organic Chemistry and also served as chairman of the editorial board. He was sought out as a member of numerous editorial or advisory boards, such as for the present Journal, Advances in Organometallic Chemistry and Organometallic Syntheses. He was editor of Volume VI and Collected Volume I of Organic Synthesis. With his *opus magnum*, "Organic Chemistry: An Advanced Treatise", in four volumes [7], Gilman conceived a collaborative, edited work that was to serve as a literary model for future comprehensive chemistry reference books: a carefully coordinated and edited sequence of chapters on important topics by recognized experts. It is a tribute to Gilman's stature and sense of collegiality that the was able to persuade various prominent research chemists to engage in this new, unprecedented publishing venture. His own chapter on organometallic compounds in this series is a model of lucid exposition and the same clarity and care are evident in the editing and cross-references of the entire treatise.

Viewed from a phenomenological standpoint, Gilman's research interests have focused on "unnatural products", that is, organometallic compounds that must be prepared and manipulated in the absence of air and moisture. Some of his most important individual discoveries have also involved "unnatural chemical behavior", by a given element. For example, the halogen–lithium exchange process (eq. 1),

which was discovered, independently, by Gilman and by Wittig in 1938 shows that the nonmetallic halogens can behave like metals in being exchanged for them [8]:

$$ArX + n\text{-}BuLi \rightleftharpoons ArLi + n\text{-}BuX \quad (1)$$

Conversely, in his pioneering research on triorganosilylmetallic compounds ($R_3Si^-M^+$, eq. 2), Gilman demonstrated that the metalloid, silicon, could exhibit nonmetallic traits very similar to those of carbon ($R_3C^-M^+$, eq. 3) [9]:

$$R_3Si^-Na^+ \xrightarrow[-NaI]{CH_3I} R_3Si\text{–}Me \quad (2)$$

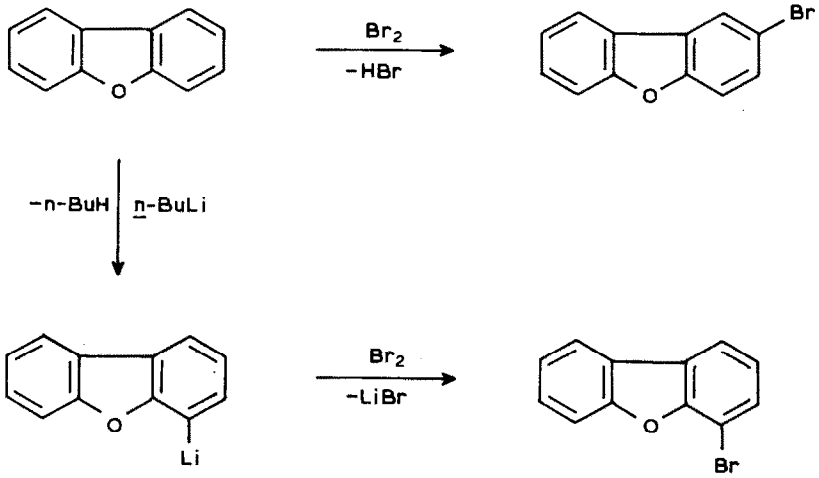
$$R_3C^-Na^+ \xrightarrow[-NaI]{CH_3I} R_3C\text{–}Me \quad (3)$$

This change in the apparent polarity of an atom in certain bonding situations has been designated in recent years as *Umpolung* [10]. Gilman's work provides some of the earliest, most telling examples.

Although the hydrogen–lithium exchange was not discovered by Gilman (eq. 4), he expanded its scope almost beyond recognition to encompass RH substrates of

$$RH + n\text{-}BuLi \rightarrow RLi + n\text{-}BuH \quad (4)$$

little discernible acidity [11]. This work drew upon another of his abiding research themes, namely the substitution chemistry of oxygen- and nitrogen-containing heterocycles [12,13]. With these substrates Gilman developed novel substitution processes based on hydrogen–lithium exchange, which led to nuclear substitution different from conventional substitution processes (eq. 5) [14].



(5)

This unique synthetic approach was also applied by Gilman to derivatives of furan, dibenzothiophene, phenothiazine, carbazole, pyridines, quinolines and acridines and has led to a host of compounds of value as pesticides, herbicides, antimalarials, antiinfectives and antidepressants. Very recently, the role of such lithiations in heterocyclic synthesis has taken on great importance.

During the latter half of his career, Gilman devoted a steadily increasing effort to the chemistry of organosilicon compounds having two or more silicon atoms in a chain or ring. In devising the various synthetic routes to such unusual compounds,

in assessing the chemical reactivity of the Si–Si bond and in developing reliable methods for structure determination, Gilman achieved the pioneering crest of his productive life [15–17]. In recognition of this, he was named the first recipient of the Frederic Stanley Kipping Award in Organosilicon Chemistry in 1962.

Threading through all these broader research themes was Gilman's continual interest in useful applications of organometallic reagents for organic synthesis. He rightly judged that the average organic chemist overestimated the experimental difficulties in working with organometallics and underassessed their value. A sampling of his efforts to correct this false impression is worth listing: (1) the preparation of hydrocarbons from the coupling of alkyl sulfonates and Grignard reagents [18]; (2) the conjugate addition of Grignard reagents to α,β-unsaturated anils [19]; (3) the formation of ketones from RLi and R′COOLi [20]; (4) the preparation of organocuprates, R_2CuLi [21]; (5) the preparation of ketones from R_2Cd and R′COX [22]; (6) the use of tetrahydrofuran to accelerate hydrogen–lithium exchanges [23]; and (7) the preparation of organolithium reagents from the cleavage of ethers and sulfides in THF [24].

His impact on chemistry has received wide recognition. The Midwest has shown its gratitude to its adopted son by honoring Henry Gilman with the Midwest Gold Metal Award of the American Chemical Society in 1951, the Iowa Award in 1951 and the Iowa Governor's Science Metal in 1977. He was the first chemist from a land-grant institution elected to the National Academy of Sciences (1945); he was chosen an Honorary Fellow of the Chemical Society of London and a Foreign Member of the Royal Society; and he was awarded the Priestley Metal of the American Chemical Society in 1977, the highest honor in U.S. Chemistry.

Perhaps the most lasting recognition and remembrance of Henry Gilman will come from the very discipline of organometallic chemistry, which he was largely instrumental in shaping in the United States. The great store of knowledge that he gathered and the many students he has inspired are his own memorial to his role in twentieth-century chemistry. Christopher Wren, the architect of St. Paul's, London, chose for his epitaph, "*Si monumentum requiris, circumspice*". Similarly, Henry Gilman could have justly said, "If you seek my memorial, look about you in the field of organometallic chemistry".

For a man such as Henry Gilman, whose zest for life stemmed from his teaching and research, he was extremely fortunate in his choice of Ruth Shaw Gilman as his wife and helpmate. Through the heavy demands of his early career and the subsequent four decades of near blindness, she was his sustaining companion and his "vision". With Henry Gilman's passing, she did not tarry much longer behind but died in March 1987. They were both survived by their two devoted children, Jane and Henry, but their daughter passed away in June 1987.

Acknowledgments

Besides drawing upon my own impressions as a doctoral student with Henry Gilman during the period, 1953–1956, I have made use of both biographical material provided by Professor David K. Hoffman, Chairman of the Chemistry Department, Iowa State University and printed sketches of Henry Gilman's career by Professors Robert A. Benkeser [25] and Glen A. Russell [26]. A complete list of Henry Gilman's scientific publications has been compiled [6].

References

1 R. Adams and H. Gilman, J. Am. Chem. Soc., 37 (1915) 2716.
2 E.P. Kohler and H. Gilman, J. Am. Chem. Soc., 41 (1919) 683.
3 H. Gilman and L.C. Heckert, J. Am. Chem. Soc., 42 (1920) 1010.
4 H. Gilman and C.R. Kinney, J. Am. Chem. Soc., 46 (1924) 493.
5 H. Gilman, in H. Gilman (Ed.), Organic Chemistry: An Advanced Treatise, Vol. I, John Wiley & Sons, New York, 1943, 2nd ed. pp. 489–580.
6 The Henry Gilman Bibliography, Chemistry Department, Iowa State University, Ames, 1020 titles.
7 H. Gilman (Ed.), Organic Chemistry: An Advanced Treatise, Vol. I–IV, John Wiley & Sons, New York, 1943, 1953.
8 R.G. Jones and H. Gilman in R. Adams (Ed.), Organic Reactions, Vol. VI, John Wiley & Sons, New York, 1951, Chap. 7.
9 D. Wittenberg and H. Gilman, Quart. Rev., 13 (1959) 116.
10 D. Seebach, Angew. Chem. Int. Ed. Engl., 18 (1979) 239.
11 H. Gilman and J.W. Morton, Jr. in R. Adams (Ed.), Organic Reactions, Vol. VIII, John Wiley & Sons, New York, 1954, Chap. 6.
12 H. Gilman and G.F. Wright, Chem. Rev., 11 (1932) 323.
13 J.J. Eisch and H. Gilman, Chem. Rev., 57 (1957) 525.
14 H. Gilman and C.G. Stuckwisch, J. Am. Chem. Soc., 67 (1945) 877.
15 H. Gilman and H.J.S. Winkler in H. Zeiss (Ed.), Organometallic Chemistry, Reinhold, New York, 1960.
16 H. Gilman, Angew. Chem., 74 (1962) 950.
17 H. Gilman and G.L. Schwebke in F.G.A. Stone and R. West (Eds.), Adv. Organomet. Chem., 1 (1964) 89.
18 H. Gilman and N.J. Beaber, J. Am. Chem. Soc., 45 (1923) 839.
19 H. Gilman, J.E. Kirby and C.R. Kinney, J. Am. Chem. Soc., 51 (1929) 2252.
20 H. Gilman and P.R. Van Ess, J. Am. Chem. Soc., 55 (1933) 1265.
21 H. Gilman, R.G. Jones and L.A. Woods, J. Org. Chem., 17 (1962) 1630.
22 D. Shirley in R. Adams (Ed.), Organic Reactions, Vol. VIII, John Wiley & Sons, New York, 1954, Chap. 2.
23 H. Gilman and S. Gray, J. Org. Chem., 23 (1958) 1476.
24 H. Gilman and J.J. Dietrich, J. Org. Chem., 22 (1957) 851.
25 R.A. Benkeser, J. Org. Chem., 33 (1968) 1.
26 G.A. Russell, The Dedication of the Henry Gilman Hall, Iowa State University, May 6, 1974.