



## Editorial

## Commentary: organic hypervalent iodine chemistry spanning three centuries—a historical overview

It is good to know not only mainstream history but also other aspects of it—especially chemical history for chemists. We should always remember Goethe's remark that 'History of science is science itself'. Additionally, a remarkable Austrian artist, Hundertwasser, was of the opinion that:

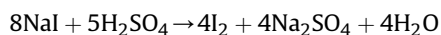
If we do not honor our past  
we lose our future.  
If we destroy our roots  
we cannot grow.

History in general and chemistry history in particular are written predominantly by gifted persons whose lives are often worth knowing along with their achievements. The history of hypervalent iodine chemistry is no exception; so in this article will be sketched briefly both the actors—the chemists—and their performance—chemistry. All those who made major discoveries promoting the relevant chemistry are included, but not people still active in the field.

### 1. Introduction: historical aspects of iodine

Iodine was isolated by the French chemist Bernard Courtois (1777–1838) who was a student of Antoine Fourcroy and Louis Thénard. After his studies, Courtois took over his father's business in Dijon—a saltpeter factory. In order to obtain this salt, i.e.,  $\text{KNO}_3$ , two raw materials were used:  $\text{NaNO}_3$  (imported or made locally from animal waste) and potassium salts derived from the ash of seaweeds. The crude product formed after leaching with water and condensation contained also  $\text{NaCl}$ ,  $\text{KCl}$ , and  $\text{K}_2\text{SO}_4$ ; treatment with sulfuric acid was necessary in order to remove various sulfur containing impurities.

One day Courtois used apparently too much sulfuric acid so that he observed a cloud of violet colored vapor with an irritating odor rising from the pan. When he repeated the reaction in a retort, the fumes condensed to dark, lustrous crystals. The substance obtained was iodine formed according to an unusual and complex redox reaction with the overall stoichiometry:



Courtois guessed that he had discovered a new element. He carried out a few simple tests, one of which was adding iodine to ammonia, with production of the highly explosive  $\text{NI}_3$ . However, he could not make a thorough study, so he told two other fellow chemists about his crystals and gave them a quantity in order to continue his work, which they did. One of them communicated the discovery to the Institute of France, without even mentioning the role of Courtois. In those days discoveries had often to be corroborated before

being published. Therefore, Joseph Louis Gay-Lussac, who was the head of the review committee at the Institute, was given a sample and so was Humphry Davy, who happened to be in Paris at the time. Working in his hotel with a portable laboratory that he had brought with him, Davy concluded that it was indeed a new element similar to chlorine. Almost simultaneously, Gay-Lussac made the same conclusion, which he announced not in a scientific journal but in a daily newspaper, on December 12, 1814. He named the new element *iode*, after the Greek word  $\omega\delta\eta\varsigma$ , which means violet.<sup>1</sup>

### 2. Hypervalent iodine

The development of hypervalent (also polyvalent and polycoordinated) iodine chemistry is characterized by an early period of intense activity, after which followed a period of stagnation, with few notable contributions. Then, in a third period, regeneration of activity was noted with interesting but not exceptional results. The fourth period, up to our days, is characterized by more and more vigorous development with a high degree of maturity. Since this last period is too close to us, there will be a minimum of discussion about it just for the sake of some of the younger generations who may consider its early years fairly distant.

First Period: 1886–1914  
Second Period: 1915–1945  
Third Period: 1946–1966  
Fourth Period: 1967–Present

#### 2.1. The first period

The first period is dominated by the German chemist Conrad Willgerodt: it starts in 1886 with his publication<sup>2</sup> of the first preparation of  $\text{PhICl}_2$  and ends in 1914 with his book epitomizing all the relevant chemistry known by then<sup>3</sup>—quite considerable. Indeed the book is packed with details about iodine compounds, some of which were coming from dissertations and were never published elsewhere. The book might still serve as a source of inspiration for the delineation of the structure of some compounds for which the original tentative structure is obviously wrong. Significantly, the book formed part of a multivolume work, indicative of the importance attached to the subject. Willgerodt produced an amazing amount of work until his retirement, partly alone and partly with the help of more than 40 students in some 60 articles and dissertations. During this period, significant contributions were made also by Viktor Meyer who unfortunately died young; in addition, worth mentioning are another German, Johannes Thiele, and the Italian Luigi Mascarelli.

### 2.1.1. Conrad Willgerodt (1841–1930)

Conrad Willgerodt initially studied natural history, especially zoology, at Braunschweig Polytechnic. Later he moved to Berlin to study chemistry; one of his professors was A.W. Hofmann. Subsequently he earned some money working in the dye industry so that he could self-finance his doctorate; that is, why he obtained this degree belatedly at the age of 34, in 1875, at Freiburg im Breisgau under the supervision of Adolf Claus on 'Alizarin and oxoanthraquinones'. Then he served for a few years at the historical Philipps University of Marburg (where the first chair of chemistry was created some 400 years ago) and finally returned permanently as professor to Freiburg. Willgerodt is best known after his name rearrangement (or the related Willgerodt–Kindler reaction), a curious sequence of events during which aryl alkyl ketones are transformed into arylated carboxamides, upon reaction with ammonium polysulfide or sulfur and an amine.

Willgerodt prepared the first compound of polyvalent (*mehrwertiges*) iodine, as he named it, in 1886: it was  $\text{PhICl}_2$  obtained through the action of  $\text{ICl}_3$  on  $\text{PhI}$ . Next year he obtained the same dichloride directly from elemental chlorine and  $\text{PhI}$ . The relevant early chemistry was developed to a great extent by himself and his numerous students culminating in the publication of the book. Willgerodt's major achievements were the preparation of iodosyl and iodylbenzenes, (diacetoxyiodo)benzene, diphenyliodonium salts, the first alkenyl phenyliodonium salt and many aryl or other analogues, e.g., from iodoquinolines. He also prepared some oxygen-bridged compounds of the partial structure  $\text{I}-\text{O}-\text{I}$ .<sup>4</sup>

### 2.1.2. Viktor Meyer (1848–1897)



Viktor Meyer obtained his doctorate under the supervision of Robert Bunsen at Heidelberg in 1867. Despite his short life (he committed suicide), he had a brilliant career serving as professor in four universities; he occupied the chairs of Wöhler and Bunsen in Göttingen and Heidelberg. He is well known for his synthetic work on nitroalkanes, oximes, sulfur compounds, thiophene, etc., whereas he also made significant studies in the field of physical chemistry. Meyer's encounter with hypervalent iodine chemistry was a brief one resulting however in six important papers published over 3 years (between 1892 and 1894). Firstly, he obtained iodosylbenzene almost simultaneously with Willgerodt and independently; both prepared it upon alkaline hydrolysis of  $\text{PhICl}_2$ . Especially interesting was the oxidation of *o*-iodobenzoic acid resulting in the preparation of *o*-iodosylbenzoic acid for which Meyer correctly deduced its cyclic structure on the basis of its diminished acidity in comparison with its non-cyclic *p*-isomer. Also, he further oxidised *o*-iodosylbenzoic acid to its also cyclic iodyl analogue (better known today as IBX). Meyer reported the first diaryliodonium salt formed in an unusual reaction from iodosylbenzene and sulfuric acid. Finally, he described the formation of

diphenyliodonium hydroxide from iodosylbenzene and iodylbenzene upon treatment with moist silver oxide.<sup>5</sup>

### 2.1.3. Johannes Thiele (1865–1918)

Johannes Thiele studied mathematics before turning to chemistry. He received his doctorate from Halle (1890) and he taught at the Universities of Munich and Strasburg. Among his discoveries are mentioned the synthesis of fulvenes and the first azirine, whereas he tried to explain the structure of benzene suggesting a 'partial valence hypothesis' and using a broken circle to represent the partial bonds. Thiele and his collaborators showed that chloriodoethylene has the ability to form several stable polyvalent iodine derivatives including a purely aliphatic iodonium salt, i.e., bis(chlorovinyl)iodonium iodide; noteworthy is the conversion upon treatment with chlorine of some iodinated acrylic and fumaric acids into heterocyclic derivatives (1-chloroiodoxolones); even iodomethane reacted with chlorine at low temperature to give an unstable dichloride. However, his claim that  $\text{PhI}$  forms a stable  $\text{PhIBr}_2$  has never been substantiated.<sup>6</sup>

### 2.1.4. Luigi Mascarelli (1877–1941)

Luigi Mascarelli obtained his doctorate in Bologna under the supervision of Giacomo Ciamician and became dozent in 1907. After a period at the University of Cagliari (1913) he was appointed professor at the University of Torino (1918). He is known for his studies in stereochemistry (recognizing isomerism in decahydronaphthalene and in hindered biphenyls) and the reactions between nitric acid and acetylenes. His contribution to iodine, in a series of 9 publications between 1905 and 1913, was the study of iodonium salts and especially the preparation of dibenzioldonium iodide, the first heterocyclic iodonium salt. It is of interest that he obtained it through hydrolysis of the tetrachloride of 2,2'-diiodobiphenyl or the corresponding bis-iodosyl analogue upon standing for some months in aqueous environment and then treatment with sulfurous acid.<sup>7</sup>

## 2.2. The second period

The second period took another 30 years during which little activity was noted, partly because of the intervening two World Wars. The work of two researchers stands out during this period, Criegee and Masson, who were the first to explore the reactivity and the mechanisms of the relevant reactions of certain compounds in some depth. Also, the first review article appeared in 1943 by Reuben Sandin.<sup>8</sup>

### 2.2.1. Rudolf Criegee (1902–1975)



Rudolf Criegee obtained his Ph.D. under the supervision of Otto Dimroth in Würzburg in 1925; he is well known for his studies with several oxidation agents (especially ozone, lead tetraacetate, peracids, osmium tetroxide) on a variety of substrates. After his

name two reactions and a compound are described: a rearrangement of tertiary alcohols, glycol cleavage, and a reactive intermediate during ozonation. His involvement with olefin oxidation and glycol cleavage led him to the kinetic study of (diacetoxyiodo)benzene and some substituted analogues with certain substrates. He published just one relevant paper in which he reported that olefins underwent bis acetoxylation, whereas glycols were cleaved to carbonyl compounds through an iodine (III) intermediate as with lead tetraacetate but more slowly.<sup>9</sup>

### 2.2.2. Irvine Masson (1887–1962)

Australian born Irvine Masson started studying medicine but he reverted to chemistry. He migrated to UK to become initially William Ramsay's personal assistant. Later he developed an interest in the history of chemistry and he wrote *Three Centuries of Chemistry* (1925). In 1924 he was appointed professor of chemistry at the University of Durham and in 1938 moved to Sheffield. Though much involved in administration, he continued research, making significant contributions in the study of physical chemistry of gases and solutions and of nitration. His brief involvement with hypervalent iodine, between 1935 and 1938, referred to thorough studies of I(V) compounds, both inorganic and organic. Masson published three papers in which for the first time the chemistry of iodylbenzene was studied systematically. Among other things, he discovered its amphoteric nature and showed its basic character isolating its salt with sulfuric acid, whereas the perchlorate proved to be extremely sensitive to explosion; indeed, he nearly lost an eye upon a violent explosion of it. The formation of unstable salts with alkalis was demonstrated by a combination of rapid measurements of solubility, conductivity and freezing point. Indeed, even in cold alkali, they changed into oxodiphenyliodonium hydroxide (and iodate), also of amphoteric character, from which he isolated its acetate, which he found to be a strong oxidizing agent. No further work has been reported since then on these interesting compounds.<sup>10</sup>

### 2.2.3. Reuben Sandin (1897–1991)

Sandin's distinguished career in teaching and research at the University of Alberta in Canada stretches formally for forty years (1924–1964) but his presence in the University started actually from 1916, as an undergraduate who received his B.A. at the age of 19. Some 200 students have taken their Ph.D. degree under his guidance. Sandin was something of a legend in the University because of his teaching quality and his friendliness to the students. He received many distinctions, among others the *Outstanding College Chemistry Teacher Award*. He published between 1937 and 1956 a total of only four papers on the reactivity of iodonium salts, including several heterocyclic ones, and on the methylation of some aromatics by (diacetoxyiodo)benzene. He was the first to discover the ability of iodonium salts to act as arylating agents (for some metals). His review (1943) helped to a better appreciation of the possibilities of iodonium salts.<sup>11</sup>

## 2.3. The third period

The rebirth of the subject during the third period, apart from the impact of Sandin's review article, was mainly due to two workers, Ken Pausacker and Frederick Marshall Beringer. In a series of eight papers, between 1953 and 1957, Pausacker established the importance of (diacetoxyiodo)benzene as an oxidation reagent. Much impetus was also given by Beringer who over a period of 12 years produced 20 papers establishing the importance of arylidonium salts as arylating reagents. A second review by David Banks, in 1966, helped to the spectacular rise of hypervalent iodine chemistry in the following decades.<sup>12</sup> Banks was among numerous people who studied chlorination using (dichloroiodo)benzene.

### 2.3.1. Ken Pausacker (1915–1955)

Ken Pausacker was a member of the lecturing staff in the School of Chemistry at Melbourne University, where as a young man he worked as a lab technician. He was a very good lecturer, popular with his students and colleagues. After graduation he worked in the industry but soon returned to University. In about the mid 1950s, in his 40's, he took unexpectedly his own life despite the fact that he never gave any indication of depression and was considered an extrovert. Pausacker's work was entirely devoted to the exploration of reactivity of (diacetoxyiodo)benzene mainly with anilines and phenols. He was the first to isolate an iodonium salt from *p*-nitrophenol.<sup>13</sup>

### 2.3.2. Frederick Marshall Beringer (1920–1994)



Frederick Marshall Beringer studied chemistry at Harvard and Columbia (Ph.D. in 1947 under the supervision of William Doering) Universities; based at the Brooklyn Polytechnic Institute, he was largely responsible for the spectacular development of the chemistry of iodonium salts, although his research interests were broader. He focused his attention mainly to diaryliodonium salts discovering their ability to act as arylating agents for a plethora of nucleophiles, identifying the mechanisms of their numerous reactions, most of them of practical importance. In a series of 20 papers ranging from 1953 to 1965 he examined systematically and in depth, with several collaborators, the physical, spectroscopic and chemical properties of a great variety of iodonium salts. He also devised several new or improved methods for their preparation, because some substrates are not universally useful for their conversion into iodonium salts, depending on the substituents of the starting materials—either arenes or iodoarenes. Of special importance was the possibility to arylate certain C-nucleophiles via free radical pathways in reactions analogous but more efficient to those of diazonium salts. The first alkynyl (phenyl)iodonium salt was also obtained by Beringer. Finally, he co-edited an inventory of all known hypervalent iodine compounds up to 1955 (427, including iodonium salts with different counterions).<sup>14</sup>

## 2.4. The fourth period

The present period is the longest and the most fertile. Indicative of this spectacular progress is that during the 21st century have been reported no less than 12 new reagents of I(V) for the oxidation of alcohols, making an impressive total of 21. One of them is the famous Dess–Martin reagent. James Martin was its senior developer.

#### 2.4.1. James Cullen Martin (1928–1999)



James Martin obtained his Ph.D. at Harvard under the supervision of Paul Bartlett; he had a distinguished career at the University of Illinois at Urbana-Champaign and lately at Vanderbilt University. His interest to understand the limits of chemical bonding led him to the landmark investigations into hypervalent compounds of the main group elements. Thus in his lab, over a 20-year period, were prepared and studied unusual structures of sulfur, phosphorus, silicon, bromine, and iodine compounds. Although most of these studies were driven by Martin's fascination with unusual bonding schemes, two compounds have found practical applications: a sulfurane proved to be a useful dehydrating agent, while the Dess–Martin reagent—presently in its third decade—has become one of the most popular oxidizing agents with wide applications in synthetic organic chemistry.<sup>15</sup>

It should be added that during this period several well known chemists have made significant contributions; among them we may refer to Nobel prizewinners Georg Wittig, Dereck Barton, Elias Corey, and George Olah. An earlier Nobelist, Paul Karrer, had also published a paper of minor importance back in 1914. It is interesting that Karrer was the first to refer to the chemistry of polyvalent iodine compounds in two pages of his classic textbook *Lehrbuch der Organischen Chemie*, in 1938.

#### 2.5. The Russian school

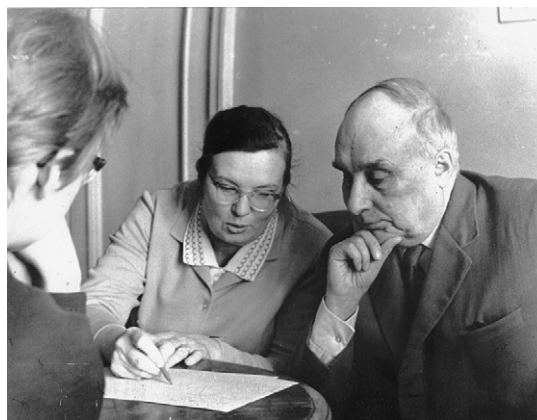
During the same period emerged the work of a number of Russian researchers permitting one to speak about the existence of a Russian school. Unfortunately, their work was published almost exclusively in Russian so that it remained relatively obscure. Starting with a leading figure of organoelement and organometallic chemistry, A.N. Nesmeyanov, who published his first paper in 1929 (preparation of a diphenyliodonium salt from a diazonium salt in small yield), several aspects of hypervalent iodine chemistry were investigated by either Russians or people coming from states of the former Soviet Union. Among them—from the old guard, deceased or retired—, we may mention E.B. Merkushev, O.Ya. Neilands (Latvian), O.A. Reutov, L.M. Yagupolskii (Ukrainian), and two women: I.P. Beletskaya and T.P. Tolstaya. A prolific researcher, academician Nikolai Zefirov (born in 1935), with significant contributions to the field of hypervalent iodine, is only mentioned here because he is still active. Generally, most work of the Russian school was done on various, sometimes esoteric, aspects of iodonium salts of many types.

##### 2.5.1. Aleksandr N. Nesmeyanov (1897–1980)

Aleksandr N. Nesmeyanov was perhaps the most eminent chemist of the Soviet era. His interests were very large in various fields of chemistry and chemical technology, but his main work was concerned with organometallic chemistry. He published

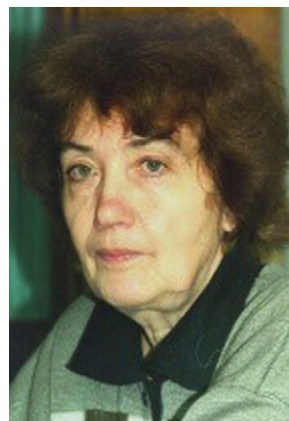
several papers on iodonium salts over a period of 50 years (1929–1980) covering many aspects of their chemistry. It is of interest that in his multivolume work *Fundamentals of Organic Chemistry* he devoted four pages on compounds mostly with polyvalent iodine and also bromine and chlorine; however, he mentioned erroneously that it was Viktor Meyer who discovered them.<sup>16,17</sup>

##### 2.5.2. Tatyana P. Tolstaya (1926)



Tatyana P. Tolstaya has been a student of Nesmeyanov with whom she published several papers. Overall, she is credited with 130 papers over a period of 50 years, from which only 4 are in English. One of them appeared in the first volume of *Tetrahedron* (1957) and was a kind of review about the reactivity of onium salts in general and iodonium salts in particular. She continued these studies with her own team until 2001. A noteworthy achievement of hers is the synthesis of mixed organic–inorganic iodonium salts with an iodine–boron bond, i.e., carboranyl(phenyl)iodonium salts, which can be regarded as unique synthons of carboranyl cations, opening new possibilities for inorganic synthesis. She published more than 20 papers on this subject, whereas she also studied the synthesis and reactivity of heterocyclic iodonium salts.<sup>18</sup> In this area she collaborated in some instances with another notable woman, I. Beletskaya.

##### 2.5.3. Irina P. Beletskaya (1933)



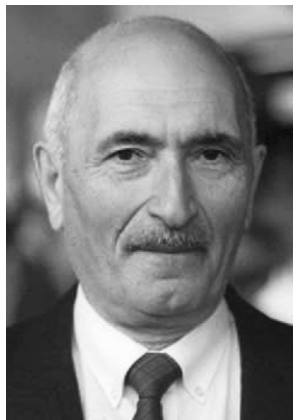
Irina P. Beletskaya is an academician and has been a professor at Moscow University (also head of the organoelement chemistry laboratory). Among her numerous achievements in various fields of organometallics, especially with lanthanides, it is mentioned that, in collaboration with Oleg Reutov, she investigated thoroughly the mechanism of electrophilic reactions at saturated carbon and other reaction mechanisms as well as several catalytic C–C bond forming reactions. In the field of hypervalent iodine she

investigated ways to improve the reactivity of the dibenziodolium cation with Pd catalysis, especially in aqueous media.<sup>19</sup>

#### 2.5.4. Oleg A. Reutov (1920)

Oleg A. Reutov was a professor at Moscow University and academician. He obtained many distinctions for his work on the synthesis and reaction mechanisms of organometallics. He was involved in both practical and theoretical aspects in many areas of chemistry. With several collaborators he investigated a large number of reactions between diaryliodonium salts and metal chlorides.<sup>20</sup>

#### 2.5.5. Lev M. Yagupolskii (1922–2009)



Lev M. Yagupolskii is credited with several substantial contributions during his long career at the University and the Academy of Science of Kiev; over 50 years he published more than 700 papers and 200 patents. Seventy five chemists obtained their Ph.D. degree under his guidance. Yagupolskii was involved with organofluorine; among other things, he found new fluorinating methods and prepared many perfluoroalkylated compounds, having developed no less than 60 new fluorine containing groups attached to various substrates. He was the first to prepare polyfluoroalkyl(phenyl)iodonium salts by several methods, one of them involving difluoroiodoperfluoroalkanes; he also synthesized some I(V) compounds and measured the sigma Hammett constants of many hypervalent iodine groups—most of them being super-strong electron-withdrawing substituents. He wrote in collaboration two reviews about fluorine-containing organic derivatives of polyvalent iodine.<sup>21</sup>

#### 2.5.6. Ojars Y. Neilands (1932–2003)



Ojars Y. Neilands a professor at Riga Technical University, discovered and developed phenyliodonium ylides, predominantly coming from active methylene precursors, over a period of many years, between 1955 and 1998. Also, he prepared first, in 1970,

a compound from iodosylbenzene and *p*-toluenesulfonic acid whose reactivity was later explored by Gerald F. Koser and is better known as Koser's reagent.<sup>22</sup>

#### 2.5.7. Evgenii B. Merkushev (1945–1988)

Evgenii B. Merkushev who regrettably died young, in his early forties, was a professor at Tomsk Pedagogic Institute. Working in isolation he was able to produce very good results. By coincidence, he described independently from and simultaneously with the author of this article bis(trifluoroacetoxy)iodobenzene, along with some important aspects of its chemistry, reported in a review article published in the form of a booklet. He wrote also another review, generally on hypervalent iodine; both articles were in Russian.<sup>23</sup>

### 2.6. The Japanese school

It seems appropriate here to mention briefly the Japanese school, which is flourishing during the last 20 years. Quite a few Japanese chemists have produced an amazing wealth of new chemistry, which was instrumental in raising the status of hypervalent iodine chemistry to its present heights. It is also fair to mention that the first company to offer commercially hypervalent iodine compounds useful as reagents was Japanese, i.e., TCI, which presently sells 29 different such reagents, some of them highly efficient and specialized. I wish to mention from this vibrant school just three persons presently retired.

#### 2.6.1. Masataka Yokoyama

Masataka Yokoyama from Chiba University, explored reactions involving free radicals, especially from various kinds of bis(acyloxy)iodobenzenes, thermally or photochemically, and also the combination of (diacetoxy)iodobenzene with halogens.

#### 2.6.2. Norihiko Yoneda

Norihiko Yoneda from Hokkaido University, developed stereo- and/or regioselective syntheses of fluorine-containing organic compounds employing ArIF<sub>2</sub>, IF<sub>5</sub>, and fluorovinyl(aryl)iodonium salts, using chemical and electrochemical methods.

#### 2.6.3. Teruo Umemoto

Teruo Umemoto from his position in Daikin Industries was largely responsible for the development of polyfluoroalkyl(phenyl)iodonium salts (FITS) chemistry; he published more than 20 papers, a review article and several patents. Some of these FITS are commercially available from Tokyo Kasei Kogyo.

Since Japan is a producer of iodine, it is interesting to mention the existence of a unique Japanese society about iodine science; its annual conferences, taking place for 10 years in Chiba, near Tokyo, cover every aspect of iodine chemistry.

It is relevant to conclude noting that the American Chemical Society has established an 'Award for Creative Research and Applications of Iodine Chemistry', in order 'to support, promote, and motivate global research of iodine chemistry and develop its use and knowledge through applications'. The award is given biennially since 2005, sponsored by iodine producer company SQM. So far all three recipients were distinguished organic chemists who published a lot in the field of hypervalent iodine chemistry, i.e., Robert Moriarty, Peter Stang, and Gerald Koser.

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Green, Herbert Morawetz and Bruce Garetz, of New York Polytechnic, about F.M. Beringer; and Professor Andrew Gewirth, of Illinois University, about J.C. Martin.

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