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HOWARD ENSIGN SIMMONS, JR.

1929—1996

A Biographical Memoir by JOHN D. ROBERTS AND JOHN W. COLLETTE

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Biographical Memoir

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BY JOHN D. ROBERTS AND JOHN W. COLLETTE

IN THE CURRENT PERIOD where almost all large U.S. corporations have downsized their research efforts and traded most of their long-term basic research for short-term gain at the bottom line, it is relevant to consider the scientific and management career, as well as the life, of one of the leading industrial research scientists of the twentieth century, who was deeply involved in the time of changing views of corporations toward basic research.

Howard Ensign Simmons, Jr., was born in Norfolk, Virginia, on June 17, 1929. His father and his uncles were sea captains, but his father did not encourage him to follow that career; instead, he helped with Howard's desire to study chemistry, starting at age twelve, by building him a small but well-used laboratory as an addition to their home. Howard's mother came from a family with a different bent. Her parents emigrated from Bavaria, and her father was an entomologist, possibly inspired by one of his forebears, Jacob Hübner (1761-1826), characterized as the first great lepidopterist, who compiled the first catalog of North American butterflies.

By his own account, Howard did not do too well in his early schooling until he encountered Latin and other languages, the study of which he found very interesting, and indeed became a lifelong avocation. He did so well at French in high school that he was offered a scholarship at the University of Virginia, but with his interest in science he decided to go to MIT. Howard saw MIT as a true Mecca of science with its aura of scientific and engineering prowess greatly enhanced by its success in war research. Howard entered MIT in 1947, joined and lived in a social fraternity, and enrolled in the ROTC. He started somewhat slowly academically, but was at the top of the chemistry class by the time he graduated.

In this period, MIT had a senior-thesis requirement and Howard did exemplary research in organic chemistry with J. D. Roberts on the mechanism of the reaction of silver salts of carboxylic acids with iodine. The head of the Chemistry Department, Arthur C. Cope,¹ was endeavoring to improve the quality and diversity of the organic chemistry graduate students and believed that the best way to do that was to require MIT undergraduates to go elsewhere for graduate work. On occasion, he was willing to relax this requirement and, in one particular period, three outstanding exceptions were E. J. Corey (Nobel Prize in chemistry, 1990), Robert H. Mazur (later the discoverer of NutraSweet), and Howard E. Simmons, Jr.

Simmons made a very successful start on his graduate thesis work in which he continued with J. D. Roberts on the chemistry of cyclobutenones. But that work was suspended so that Howard could investigate the intermediacy of benzyne (benzene minus two hydrogens, C_6H_4) by the removal of HCl from chlorobenzene with the strongly basic reagent, sodium amide. Howard played a crucial rule in this achievement, which is immortalized in almost every elementary textbook, not only as evidence for benzyne but also as a prime example of the use of isotopic labeling to establish a reaction mechanism.



When his thesis supervisor decided to move to a professorship at the California Institute of Technology, Howard elected to remain at MIT and complete his doctorate work with Arthur Cope on cyclooctane chemistry. In all, Howard's Ph.D. research resulted in six publications in quite diverse fields of organic chemistry.

Although he would have been a prime candidate for a postdoctoral fellowship or a junior academic position when he finished his Ph.D., Howard accepted a position in the Chemical Department (subsequently the Central Research Department) of the DuPont Company in 1954. This was during a period later referred to as the golden age of basic research at DuPont. At that time, the company had wellestablished businesses in fibers (nylon, Dacron[®], Orlon[®]), films (cellophane, Mylar®), plastics (polyethylene, Teflon®), neoprene elastomer, tetraethyllead, automotive finishes, refrigerants, and many basic chemicals, as well as owning more than 20% of General Motors Corporation. The success of the research of Wallace H. Carothers² before World War II with nylon, along with the demonstrated utility of what had been considered purely academic research to the war effort, spawned a euphoria of what basic research could achieve at DuPont's industrial laboratories in the way of "Better things for better living through Chemistry." In this period,

well before the magnificent array of DuPont products became commonplace, the company was clearly ensconced in the public's mind as a provider of technological miracles.

DuPont's research in the early 1950s when Simmons came aboard was by no means concentrated in the Central Research Department. Absolutely outstanding exploratory research was being carried out in the Organic Chemicals, Polychemicals, Explosives, Photo Products, Pigments, Textile Fibers, Agricultural Chemicals, and Electrochemicals Departments that were the mainstays of DuPont's businesses. And much of that research was published or presented at professional meetings.

The success of the research in the manufacturing departments in support of their businesses, along with an upper management decision to make Central Research independent of the operating departments, provided Central Research the opportunity to engage in many basic research programs that became the envy of the university chemical community. This is not to say that Central Research programs failed to be directed toward new businesses for DuPont. The objectives were in place, but a principal focus was taken on the development of new chemistry, rather than incremental improvement of existing processes.

The emphasis on entirely new chemistry was surely inspired by a number of extraordinary discoveries that shook up conventional ideas of what was possible in organic chemistry. One was the discovery in Germany of cyclic polymerization of acetylene to provide any desired quantity of cyclooctatetraene, a substance made earlier in very small amounts that turned out later to undergo a plethora of quite unexpected chemical transformations.



Another was the unusual properties found for highly fluorinated substances. Still another was the discovery in England of ferrocene and its wholly unanticipated properties. Ferrocene was later shown to have a structure with an iron atom sandwiched symmetrically between two five-membered carbon rings.



This latter finding led to an entirely new field of organometallic chemistry that has produced many new catalysts for diverse reactions of prime industrial utility. In this arena, DuPont played a very significant role.

As we have said, the goal of DuPont's Central Research in this yeasty period was to produce new chemistry and new chemicals. Particular emphasis was to be placed on organic chemicals and, in one way, this was particularly appropriate, because before and until a few years after World War II, research in organic chemistry did not require substantial capital investments. This was true despite enormous growth in the knowledge and utility of organic chemistry, as well as the development of new reactions, because little change in the techniques available for characterization or handling of organic chemistry had occurred over the previous fifty years.

But, unforeseen and enormous changes were in the wind. One was the ongoing development of highly sophisticated techniques applicable to the analysis of organic compounds, such as visible and ultraviolet spectroscopy, gas- and liquidphase chromatography, mass spectroscopy, routine crystallographic structural analyses, infrared and Raman spectroscopy, and, perhaps more than any other, nuclear magnetic resonance (NMR) spectroscopy.

Central Research, by virtue of its charter, sought to be in the forefront in investigating these techniques and demonstrating their value for industrial research. With NMR, DuPont played a major role in the development of its uses for analysis and structural characterization, primarily through the work of William D. Phillips.³ Instruments of this character, while enormously increasing the efficiency of organic research, require investment of millions of dollars in technologies utilizing equipment that becomes essentially obsolete and needs to be upgraded or replaced in three-to five-year cycles, much in the same way as many of us continually encounter on a smaller scale with personal computers.

Additional research costs also resulted from greater emphasis on laboratory safety, an area in which DuPont has always maintained a leadership position, as well as changes in laboratory practices designed to meet societal concerns for emissions and disposal of laboratory wastes.

These and other problems were to confront Howard Simmons in his steadily upward career at the Central Research Department. However, early on, the focus was on synthesis and study of entirely new compositions of matter, although perhaps with some degree of overconfidence that profitable uses could be found for these materials as they became available. Right from the outset, Simmons developed new chemistry. His early work featured a keen interest in using highly reactive intermediates in synthesis. He had found a reference to the formation of a gas in the reaction of CH_2I_2 with zinc and investigated the possibility that the gas could be ethylene, $CH_2=CH_2$, formed by dimerization of unstable carbene, CH_2 . A detailed study of the reaction led to a very general synthesis of cyclopropanes, derivatives of the three-membered carbon ring, $(CH_2)_3$, now universally known as the Simmons-Smith reaction. One of Howard's collaborators on studies of the mechanism of this reaction was E. P. ("Doc") Blanchard, who later became a vice-chairman of the company.



Simmons-Smith reaction

A later project involved further elucidation of the structure of benzyne and, to this end, he conducted trapping experiments of this very unstable intermediate that led him to conclude that benzyne is truly aromatic in the same sense as benzene, but has a very reactive multiple bond. This conclusion remains the prevailing view to this day, although much more is now known about benzyne, and even its NMR spectrum has been taken.⁴

A discussion of some elements of the culture of DuPont's Central Research Department in Howard's time is perhaps worthy of mention here. One still adhered to is that research chemists (often designed as "bench" chemists), with very few exceptions, carry on their work with the assistance of technicians possessing different levels of skill and experi-

ence. Normally, there is no way for chemists at this level to multiply their research output by having more than one technician. Promotion to research supervisor is necessary, and then the chemist acquires an office and a research group that works on the supervisor's ideas to quite varying degrees. Much depends on the research credentials of the supervisor, and in Howard's case they were very high. Many of those who came to CRD often decided that their chances for promotion and influence in the company were better if they transferred to an operating department, and this meant that the turnover was relatively high, which of course gave more opportunities for the department to search for and hire outstanding new Ph.D. recipients.⁵ In recent years, transfers have become less common and, as a result, with the slowdown of hiring generally, the average age of the CRD personnel has risen considerably. At the same time, more technical responsibility for the direction of research has shifted to the chemist as the result of having to carry out short-term projects in support of the company's business units.

An open-door policy was also a feature of the Central Research Department culture when Simmons came. This meant that, even up to the research director, everyone's door was kept open at all times unless confidential matters were being discussed. It was a great policy for ready communication and good feelings, but not so satisfactory for contemplative study of difficult problems. Simmons made a conscious and successful decision on his own to change the culture. It was not altogether popular with the management, but he was so good that he made it stick. Despite this, all of his colleagues regarded him as being very accessible and helpful with their problems.

Another consideration for Central Research was publication policy. It is customary for industrial research laboratories to be wary of publication in the open literature, and many in DuPont opposed CRD's quite vigorous policy of displaying its technical achievements at scientific meetings and in the scientific literature. Some take the view that, even if publication does not actually aid a competitor's development or improvement of a commercial process, open publication could give valuable indications to a competitor as to where DuPont's research was heading. Further, there is the question of compromising patent protection, and, in Howard's case, the opportunities to patent the Simmons-Smith reactions were in fact limited by early publication of the results.⁵

To reconcile the concerns of the operating departments with regard to the importance given to publication by CRD management, a system was established of circulating proposed publications to the operating departments for nonobjection to, if not outright approval of, before sending the manuscripts to journals.⁵ There can be no doubt that the Central Research publication policy was a fabulous success for recruiting talented young chemists. During the period when Simmons was active, many graduate students believed that the best research positions anywhere that one could aspire to were at the very few top universities and DuPont's Central Research.

Another sticky issue that Simmons helped to resolve regarded whose names should appear as co-authors on CRD publications. Some of the supervisors who did not actually participate in particular research projects but had administrative responsibility over them, felt that they should be included among the authors. This did not sit too well with the chemists directly involved and a practice was established to include only those who actually participated. It was true, however, that if the author(s) wished, others could be afforded courtesy authorship.⁵ A wonderful international relation-building policy carried out by CRD during the Simmons era was to invite foreign chemists to come to the United States, not only to visit CRD but also to spend some time with university chemistry departments giving lectures and getting acquainted. Simmons made visits to Europe to search for the rising research stars to implement this policy, which developed many long-lasting relationships.⁵

As research supervisor, Simmons continued the study of unusual intermediates—now of cyanonitrene, a substance formed by heating cyanogen azide.

Cyanonitrene was found to provide access to a variety of cyano-substituted products by addition to aromatic hydrocarbons, alkanes, and alkenes. Simmons used isotopic labeling to show that cyanogen azide reacts with alkenes before losing N_2 , but with aromatics and alkanes, cyanonitrene with two chemically equivalent nitrogens is the intermediate. Further, he demonstrated that cyanonitrene is initially formed in a singlet state and then decays with a measurable half-life to a more stable triplet state.

During the 1960s and 1970s, the Central Research Department had an extensive program under the direction of T. L. Cairns to synthesize long-chain cyanocarbons, substances analogous to long-chain fluorocarbons, such as Teflon®.



In a variation on this theme, Simmons recognized the potential of disodium dimercaptomaleonitrile for preparation of polycyano compounds, and he and his research group made many novel substances of this type, including tetracyanothiophene, tetracyanopyrrole, and pentacyanocyclopentadiene.







tetracyanothiophene





Simmons also made a major contribution to the mechanism of cycloaddition reactions by providing the first example of a nonstereo-specific polar [2+2] cycloaddition by way of an intermediate zwitterionic intermediate.

Some of his most interesting experimental work was in his study of flexible bicyclic diamines. This research was stimulated by the classic study of DuPont's Charles Pedersen⁶ on crown-ether complexes. The bicyclic amines made by Simmons and Park had the unique property of *in-out* isomerism, where a chloride ion can be encapsulated or not in the hydrocarbon cavity, depending on pH and the numbers of carbons connecting the nitrogens.



macrobicyclic amines (n = 6-10)

Along with the foregoing, Simmons made important contributions to theoretical chemistry. Early on, with the aid of DuPont's Rudolph Pariser, Simmons became involved in quantum mechanics, especially molecular orbital theory applied to the spectral properties of conjugated π -election systems. He used his theoretical techniques to gain fundamental understanding of the stereoisomers (substances with the same general connections between the atoms but with different geometrical arrangements) of planar, linear, and cross-conjugated polyenes, as well as the cyclic radilenes. He gave much attention to the molecular-orbital interactions in three-dimensional space, and this work led to the concepts of spiro-conjugation and trefoil aromatic compounds. His interest and skills in mathematics were evident in his work on the D_{9h} symmetry point group and the diamond-lattice analysis.

The chemical community has been fascinated in recent years by the discovery and chemistry of the caged allotropic forms of carbon known as "buckyballs." It is interesting as further evidence of the Simmons imagination (if any is needed by this point) that there exists a memorandum submitted to T. L. Cairns by Howard Simmons and Edward L. Jenner on September 7, 1956, entitled "Dodecahedrane. An Unprecedented Structural Type." This memorandum lays out in exquisite detail the anticipated geometry, the interesting question of expectations of the properties of compounds capable of encapsulating a void, as well as an imaginative projected synthesis of the $C_{20}H_{20}$ dodecahedrane by way of dimerization of a bowl-shaped tricyclodecatriene (later dubbed "triquinocene")—a route that was conceived independently by Harvard's Robert B. Woodward, but which turned out in both DuPont's and Harvard's hands to be unsuccessful despite the efforts of enormously talented Tada Fukanaga, who worked with Woodward and then moved to CRD to continue research on the synthesis. Much later, dodecahedrane was made by a wonderful but far more elaborate synthesis by Paquette and co-workers.⁷



dodecahedrane

It was in the character of Howard Simmons that, as his responsibility for research management increased, his interest in theoretical chemistry did not diminish and he developed novel concepts for applying finite topology to problems of molecular structure. With the collaboration of R. E. Merrifield, this work probed direct relationships between mathematics and chemistry. The key elements were the development of combinatorial analysis of the structures of finite spaces and the associated graph-theoretical analysis. He found the first-known method of describing the structure of a molecule by means of a topological space in a well-defined manner. It was further shown that combinatorial analysis of topological spaces provides a quantitative description of molecular complexity, as well as a detailed description of bond-strength variations with molecules that agrees well with quantum-mechanical calculations. The result of his collaboration with Merrifield was an extraordinary monograph, *Topological Methods in Chemistry*, published in 1989 just two years before he retired.

The account of the scientific work of Howard Simmons is given in greater detail than might be interesting to the general reader, because it shows the character and scientific culture of the Central Research Department in the forty-year period starting about 1950. Simmons was not an aberration in Central Research; other path-breaking scientific work was accomplished by T. L. Cairns, William D. Phillips, Earl Muetterties⁸ and George Parshall, to mention just those of Central Research who were elected to the National Academy of Sciences.

Let us turn now to the important contribution made by Howard Simmons in the management of the Central Research Department. Howard had a prime role in enlarging the already significant impact of the Central Research Department. He became research director in 1974 and vicepresident of Central Research in 1979. Under his leadership, the scientific effort of the laboratory was broadened and expanded with new thrusts in life and materials sciences. The thrust into life sciences was initiated by the then chairman and chief executive office of the company, Edward G. Jefferson, and resulted in a doubling of the research personnel in the department. A powerful basic research group in molecular biology was assembled that later was a major attraction for Merck and Company to participate in the formation of the joint pharmaceutical venture DuPont-Merck Pharmaceuticals, which for a few years had many DuPont and DuPont-Merck personnel working side by side in the Central Research laboratories.

The thrust into materials science was characterized by research on new polymers, optical and electronic materials, high-temperature superconductors, and ceramics. These new efforts were carried on while maintaining strong core efforts in exploratory organic chemistry, physical chemistry, analytical techniques, and catalysis. The expansion is evidenced by the scientific publications of the department, which increased from an average of 100 per year during 1975-79 to 200 per year during 1985-87, with major growth in biological and material sciences.

During the Simmons period as research director and vicepresident, the department played a critical role in developing practical catalytic processes to make hydrochlorofluorocarbons (HCFCs) to replace the chlorofluorocarbons (CFCs) implicated in atmospheric-ozone depletion, an important societal need. Central Research was able to respond because of its scientific depth in fluorocarbon chemistry and in catalysis.

In the polymer field, group-transfer polymerization was discovered by O. Webster⁹ and was the first new polymerization process developed since living anionic polymerization. Not only was the mechanism of the reaction determined, but the process was converted to commercial application in a relatively short time. The basic process of group transfer also has application to general organic synthesis, including natural products. Other studies have involved extension of theoretical modeling to predict tensile properties of flexible- and rigid-chain polymers.

The department developed new electronic and magnetic materials, especially potassium titanylphosphate, a most versatile nonlinear optical material. A major program was also carried on for the synthesis, characterization, and application of high-temperature superconductors.

Molecular biology and agricultural biotechnology also received major attention, one output being advances in DNAsequencing technology based on synthesis of novel fluorescent labels. This effort also resulted in Qualicon, a DuPont venture that identifies bacteria by examination of their DNA using PCR. Substantial success was also achieved in the synthesis of unnatural peptides and proteins to accomplish specific functions and prediction of their tertiary structures.

DuPont was the first chemical company to obtain a Cray supercomputer and was in the forefront of use of supercomputer applications in quantum chemistry in support of basic research, atmospheric models relevant to ozone depletion, and theoretical models of material properties in complex multiphase systems.

Over the forty years of the golden age of DuPont's basic research programs in the Central Research Department, the world was changing. New generations of the general public came to regard nylon, Teflon®, Dacron®, Mylar®, and so on, not as technological wonders but as commodities just as essential to modern life as food, water, and power, but desired to be inexpensive, completely benign to human health no matter how used, and produced by environmentally benign processes. However, as patents expired and expertise in polymer technology became more widespread, global competition increased. Many more research-based companies entered the polymer field and new polymers aimed at niche markets proliferated. Still other companies entered the field by purchasing turnkey plants to manufacture nylon and polyester. They could then compete with DuPont on a cost basis without making DuPont's large investment in research and market development. To be sure, many such operations lacked the technical savvy to provide the

quality of DuPont's sales-service support, but many customers are willing to sacrifice quality of support for lower prices.

With the rise of rampant and global competition along with a squeeze on profits and higher energy and environmental costs, it was clear that DuPont upper management was sure to ask, "What has all of this investment in Central Research done for us?" Phrases like "research is a black hole into which you pour money" became common. One should not infer that the value of the work of Central Research to the company's bottom line was not questioned earlier. Indeed it was, and often. Notions that DuPont has had during the last half of this century an unwavering corporate strategy for the utilization of its research in supporting existing businesses and starting new ones do not square with the facts.¹⁰ The company, driven by rapidly changing business climates in the last thirty years, has often been in internal upheavals, with multiple periods of reorganization swinging between concentration, on one hand, on profit centers, strategic business units, and the like and, on the other hand, to selling off existing businesses, new acquisitions (the largest, Conoco), and new ventures.^{10,11} Research has always felt the swells from these disturbances, but for a long period these were moderated, because upper management very largely had technical rather than business backgrounds and recognized the need for patience when the lead time between a laboratory discovery and a plant turning out a product is often ten to fourteen years.

It is certainly true that many new DuPont products were brought to the market between 1950 and 1980. To mention just a few, there were Nordel®, an oxidation-resistant elastomer; Lycra®, the popular spandex fiber; Delrin®, polyacetal polymer; Viton®, a fluoropolymer elastomer; Kevlar® and Nomex® aramid fibers; Kapton® polyimide films; and titanium dioxide paper and paint whiteners. Although of high quality and successful, these did not instantly capture the public imagination like nylon.^{2,12} Instead, these products were born into an already crowded arena of polymers, made worldwide and, to a substantial degree, they had to compete primarily in niche applications.

The failure of the Central Research Department's overabundance of extraordinary new chemistry to provide a cornucopia of stunning new products that could be commercialized by the operating departments at acceptable costs and in acceptable time periods, along with the need to make the manufacture of the company's existing line of products more efficient and more environmentally benign, as well as perceived needs for better returns on stockholders investment, led to many changes. Initially, a virtual hold occurred on new hires in Central Research, then substantial downsizing and a refocusing of the research effort on immediate, rather than long-term, concerns.

Simmons was already involved in management when Irving Shapiro, a lawyer, became the head of the company and, when faced with the Arab oil crisis and escalating raw material costs, made substantial cuts in research. Business conditions were better when Shapiro was succeeded by Edward G. Jefferson, a Ph.D. chemist, who was a strong supporter of research and, as mentioned above, brought about a very substantial expansion of CRD in life sciences. But this was not of itself a panacea for those chemists and supervisors who felt threatened by expansion into areas in which they were unfamiliar. Simmons presided over CRD through several of the ups and downs of changing views of the value of basic research and did his very best to defend the work of the department, as well as to try to accommodate to the new situations. However, after his retirement, he often expressed private dissatisfaction with the extent to which the mission of the department changed to focus on

short-term gains, and this exacerbated his concern for DuPont's long-term future.

Howard Simmons was an extraordinarily interesting person with a quickness and intellectual power that was truly impressive. He had more than enough requisites to be successful in the academic world, but he refused a number of offers of university professorships, including MIT. He did participate in visiting professorships at Harvard and the University of Chicago, and he accepted an adjunct professorship at the University of Delaware. He took professional responsibilities seriously, and served on advisory or executive committees for the American Chemical Society, MIT, Harvard, Rensselaer, Franklin Institute, Los Alamos, Maryland, University of California at San Diego, and Chicago. He was on the Advisory Board and later president of the Board of Trustees of the Chemical Heritage Foundation. Late in life, he was appointed to the National Science Board, but ill health reduced his participation in the last part of his term.

Simmons's scientific and management work was recognized by honorary degrees from Rensselaer and the University of Delaware. He received the Chandler Medal from Columbia, the National Medal of Science in 1992, and in 1994 both the Priestley Medal, the highest award of the American Chemical Society, and the Lavoisier Medal of the DuPont Company, its highest award for technical achievement. He was elected to the National Academy of Sciences in 1975 and the American Philosophical Society in 1990.

Howard was a staunch political conservative with a high level of disdain for most contemporary liberal thought. One could have almost bitter arguments with him on matters of political principles and outcomes, but, because these were on an intellectual rather than personal plane, one could remain a warm and fast friend. An omnivorous reader, Howard was extraordinarily well informed on a wide range of subjects.

From age twelve onward, Howard Simmons and Elizabeth Warren grew up together in Norfolk. After the notunusual teenage ups and downs, they were married on September 1, 1951. Liz, as she is widely known, was a wonderful partner in the Simmons enterprise. The couple had two sons, John W. and Howard E. Simmons III, both of whom earned Ph.D. degrees in organic chemistry, John at Yale, Howard at Harvard. They are employed at DuPont, John in DuPont Nylon and Howard at Central Research.

Howard Simmons' views on physical exercise were apparently not far from those of Alexander Woollcot's: "If I think about exercise, I know if I wait long enough, the thought will go away." But he did have a good-sized powerboat and found great happiness in overnight cruising on the Chesapeake Bay. A heavy smoker for much of his life, Howard finally succumbed after a long struggle to lung cancer and heart disease on April 26, 1997.

Howard Ensign Simmons, Jr., was a titan among chemists and his personal and scientific achievements will not soon be forgotten.

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12. For vivid descriptions of the public reaction to the initial sales of nylon stockings, see preface in Note 2 and pp. 268-71 in Note 10.

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