



Chemical reminiscences

Gilbert Stork

Department of Chemistry, Columbia University, New York, NY 10027, USA

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1. Part 1. My chemical journey

I was born on December 31st 1921 in the suburb of Brussels, known as Ixelles. My father was a Belgian citizen and my mother was French. Shortly after my birth, my parents left for Paris where we lived in an apartment, 1, rue de la pompe. This was in an area called La Muette where there was a wooded area with a closed street where one could skate on four-wheeled metal skates that could be attached to one's shoes. I remember also that in the area there was a 'guignol', a small structure in which skilled performers manipulated string puppets to tell stories of cops and robbers for the amusement of the young audience outside. My father was the middle of three brothers who had taken over a jewelry store that had been started by their father, who had died relatively early, and whom I had not known. My father's role was to work from an office in Paris to purchase jewels, which would then be resold by the other two brothers, Sylvain, older, and Alex, younger than my father, in the family store in Brussels, or its summer equivalent in Ostende. My mother was from Nancy, in the North Eastern part of France called Lorraine. Her parents were the only grand parents I knew. They lived in Nancy where my grandfather dealt in insurance. I had a brother, Michel, who was 2 years my junior, but he died of a middle ear infection when he was three (there were no sulfa drugs or penicillin then). I had a sister, Monique, about five years younger than I, who still now lives in France, in the south-eastern city of Carcassonne, where she has a house. We were always very close and have remained so.

We spent the summer at the beach near Ostende, when I was quite young. There I fished for shrimp with a small hand pushed net, in the pools left by the receding sea, or built sand castles in the hope of winning a prize—which I never did. Sometimes, I rented

a donkey for 15 min or half an hour, and ran up and down the beach, while the boy in charge of the donkey trotted along. This was inconvenient because whenever I was ready for the donkey, it was often taken, and I had to wait my turn. I profited from the absence of my parents who had gone for a few days visit to Paris, to convince my uncle Alex, who was supervising me, to buy a donkey for me. He was easily convinced of the wisdom of the operation, and proceeded with it. This did not work out as well as I had planned. The donkey passed the time by eating my hair, which was straw colored, and it turned out to be not so easy to arrange for feeding the donkey, and for lodging it for the night. Fortunately, my parents soon returned and arranged for the return of the donkey to its previous owner, and all returned to normalcy.

I do not recall much of my early education. I was taught to read at home, by my mother. I have few recollections of going to a private school class where, among other things, I tried to learn the mechanism by which water was brought up from a well in response to the working of a pump. I then attended a public institution, the Petit Lyée Janson de Sailly about a mile or so walk on the rue de la Pompe. I was there for three or four years. I do not remember what went on there except that, outside of it, I used to engage in races on a friend's bicycle to see who could go faster to the end of a street 1/3 mile away and back. One had to cross over a horse alley to return, and this was my undoing. I crossed, not noticing a car—I still see the large V on the hood of the Citroen, which threw me off my bike. The two policemen who brought me home, bleeding from a cut in the leg, created quite a shock in the Paris apartment. I remember that my sister, especially, could not keep from being quite sick when seeing me bloody between two policemen.

I attended the adjacent Lycée itself, until when I was about 14, my parents moved to Nice, in the south of France. I finished my secondary school at the Lycée de Garçons of Nice, until it was time to take the feared 'baccalauréat' examinations. These were in effect the entrance examinations for the Universities, and also the

E-mail address: gjs8@columbia.edu

necessary requirement for the preparatory classes for the 'Grandes Ecoles', such as Normale Supérieure, Polytechnique, etc. To my surprise, I passed the baccalauréat exams on the first try, one of about 30% of the candidates who did so. But there was still one more year of 'philosophy' for those not wizards in mathematics. This ended in a second baccalauréat, which I passed with some distinction.

During all these years I remember only two classes, French and Chemistry. French, I was very good at, and was chosen to represent my high school in the 'Concours General' in which competitors chosen from the whole of France wrote essays on subjects sent from Paris. I did not win anything. Chemistry, I recall, was taught by a very good teacher.

By the time I passed my second baccalauréat it was 1939, and clouds of the second world war were gathering. My parents became very concerned because we were of Jewish origin, even though I cannot remember anything relating to religion with my family, and did not enter a church or temple, except when attending a wedding, at least from the age of thirteen. They made the obviously difficult decision of leaving France for the US. This is how, in the fall of 1939, I found myself on a boat, which was headed for New York from the port of Bordeaux, together with my parents and my sister. The decision to go to the US was facilitated by the fact that my father's older brother, Sylvain, had emigrated to New York already, some time earlier, and that I had finished my secondary schooling.

Anyway, we arrived in New York, and ended in a hotel on Broadway, the Hotel Lafayette (it no longer exists), and I started contemplating that I should go to college somewhere. Starting from the false assumption that all colleges were equivalent, I studied, in the New York public library, pamphlets issued by the U.S. department of education (woefully out of date).

I concluded that the combination of low cost and good chemistry made the University of North Carolina a clear winner. Unaware that one had to apply for admission (!), I therefore took a bus for North Carolina. I was disappointed to find that the University of North Carolina had a quarter system, and that the weather was not so great (this was December), so I went back on a bus that, this time, terminated in St. Petersburg, Fla, a destination selected by my parents who got a house there, and I prepared to enter the University of Florida, in Gainesville, for the second term that started in February. During the weeks that preceded my going there it was decided that auditing classes at St. Petersburg Junior College would be a good use of my waiting time. So, I arranged to audit a class in speech. This was not very successful. I searched for a topic, and decided to tell the story of Evariste Galois' last day. This mathematician was only twenty one years old and had been challenged to a duel by someone who claimed he had been making eyes at his wife. Sensing that he would be killed the next day, he spent the night scribbling mathematical notes, interrupted by numerous 'I have no time', and was indeed killed the next day. Somehow Galois' notes were saved and later published by the great mathematician Gauss who realized their relevance. They became the source of extremely important mathematical tools. A great story, that I decided to tell. It was very disappointing when I found out that none of it had been understood by my audience. Another happening was much more favorable. I met, at the Junior College, a young lady for whom I opened a door when she was leaving the school, a gesture that was apparently so unusual that, together with my accent and strange clothes, I made a very favorable impression. In any case, she and I got married a few years later! I was a graduate student in Chemistry at Wisconsin, and she had finished her studies to become a teacher, at Washington University in St. Louis.

But back to school. I entered the University of Florida, as I had planned, for the second semester of 1940. The wisdom of selecting to concentrate in Chemistry rapidly became evident: examinations were based on true or false statements, and did not demand

speaking. Even though the course required exams that included the whole year, thus including the first semester, which I had not taken, this turned out to be quite manageable, except for a small point. I had never visited the lab, except for checking in. I thought the lab was to find answers to questions if one did not already know the proper answer. Anyway, this led to my getting an 'Incomplete' for the course. After some argument, I convinced the management to change the grade to a C, which avoided having to pay \$16 as a fine for getting an 'Incomplete' (about \$250 in today's money!).

My academic career was almost terminated when I had gone to Jacksonville to meet my future wife, who had come there from St. Louis. There had been a story of a German submarine that had deposited some spies during the night, and police was checking on people who looked like foreigners. For some reason, they stopped me. They checked on the truth of my stating that I had been in the States for some time already, by asking me who had won the World Series. I had no idea of anything connected to baseball, but I vaguely remembered something I had heard on a radio, and blurted 'St. Louis Cardinals'. That apparently was right, and the police let me go.

A great thing happened while I was at Florida: I was in the 'library', a little room with few books. I took a copy of a bound 'Chemical Abstracts', opening it at random. It fell open on a page that showed the structure of the alkaloid quinine, and suggested that some German chemists were attempting to put it together. This was a revelation. One could try to put together—synthesize—substances one had found in nature, once their structure was known. I found this fantastic, and quinine remained a goal for the rest of my life. Indeed, I started right there trying to synthesize quinine in a lab, which the faculty let me have, since no one else used it. This had almost a bad end when I decided to use β,β -dichloroethyl *N*-methylamine as starting material, not knowing that it was 'nitrogen mustard', the analog of mustard gas. I stopped work with it when my right hand became so swollen that the fingers could hardly be seen any longer. I returned to normalcy after some time.

I was quite happy at the University of Florida, but the Professor of Physical Chemistry succeeded in convincing me not to stay there for my Ph.D. I decided that Illinois would be a good place since Roger Adams, the head of the department, was someone who had worked on piperidine natural products, and that was related to quinine. Unfortunately, when I reached the outside room of Adams' office, where the secretaries were typing away, I was told that, without an appointment, I could not see Dr. Adams. I was shocked. I now realize that one had to apply to a department in a somewhat more formal way, but, then, I was annoyed. I went to the bus station, and took a bus going to Madison, Wisconsin, where a former student of Adams, Samuel McElvain was teaching. He happened to have worked extensively on pyridines, and I thought that was close enough to the required piperidines.

I recognized later that the normal reaction of an experienced chemist to the document I presented to Professor McElvain, outlining the steps I wanted to study on my way to quinine, would be prolonged laughter. McElvain, however, said 'something can be done with this' as he returned my quinine synthesis plan. In any event, I was assigned a place in a two person lab, on a floor above McElvain's office, and started to work. I must explain that I thought the Ph.D. required one to work independently, and so, when I decided that quinine could wait a little, and that I would start on biotin, I did not inform McElvain. Biotin had its structure established by Professor Du Vigneaud, at Cornell, a short time before. My planned synthesis was very nice, making first the aromatic furan analog, which could be anticipated to be hydrogenatable to the all cis compound. This would be the tetrahydrofuran analog of the tetrahydrothiophene, which was biotin. Transformation to biotin would then involve HBr opening and inversion of the dibromide with sodium sulfide, a double inversion, which would return the biotin all cis arrangement. Unfortunately, or perhaps fortunately,

McElvain, on his annual visit to the floor above, could smell hydrogen sulfide rather than piperidine with which I was supposed to work, and he moved me to a lab next to his office where he could follow more closely what I was up to. The work I had done resulted, however, in my first paper, a 'Communication to the Editor' on the 3,4-diurethane of furan. This paper is interesting not only because I was its sole author, but because its single melting point was corrected by an unusual 'communication from the author' to Chemical Abstracts.

So back to quinine. My work was interrupted by a temporary setback that, in fact, proved greatly favorable. I was supporting myself at Wisconsin by being a teaching assistant whose duties were to oversee a group of army soldiers in the laboratory. My section had problems. It was in a ground level laboratory that meant that some of my twenty or so people would be caught smoking outside. Then there were an unusual number who forgot the key to their lab locker and had to get it opened by a stockroom assistant. The punishment, seriously contemplated by the overall manager of the undergraduate laboratories, was to take points away from one of the examinations, a decision to which I strongly objected. Then, some of my charges escaped through the windows from the lab so as to get in line for lunch a little earlier than waiting for the bell to signal the end of the lab period. The manager was not amused. He had, after all, sent in one of his assistants to block the door until the bell would ring. When I did not respond to a request that I name those leaving through the window, which I could not do, because I did not know their names, my lack of cooperation was taken for insubordination. But what finally did me in was a greater apparent misconduct: I was tired to see my section always do poorly in exams, so I decided to do something about it. I believe that I extended the use of 'flash cards' to chemistry from their use for things like foreign language, which required no thought. I prepared a set with, for example, $Zn+H_2SO_4$ on one side of a card, and $ZnSO_4+H_2$ on the other side, and had them all copy the set, and showed them how to use it. The result was that my section got the highest grade on the next test, a fact that was taken to mean that I had given the answers to my charges ahead of time. To make this story short, I was called in the office of the physical chemist chairman of the department, and told, in the middle of the semester, that 'some people can teach, and other people cannot', and I was terminated. This was serious. I recall that I went to McElvain with the news. I will forever remember his reaction to my story. He roared with laughter, and arranged for me to get a research fellowship!

Wisconsin was also where I met Carl Djerassi, who was working with Professor Alfred Wilds for his Ph.D. His laboratory was rather far from mine, but we made it a habit to bring our lunch in paper bags and to eat it together in my lab. I convinced Carl to work for me, a few hours a day on a synthesis of morphine that was vaguely related to his work on the synthesis of cyclohexadienones. The first step was the methylation of 2-formylcyclohexanone. A paper had recently appeared in which, starting with 2-formylcyclohexanone, and without any resolution, the final compound, santonin was obtained, and claimed to be identical with the natural product in all respects, including rotation. This meant that the first step had to have taken place to produce optically active 2-methyl-2-formylcyclohexanone! I remember that we made models, with Fisher balls and sticks, and ...yes, this seemed possible. Carl was talked into repeating the methylation of 2-formylcyclohexanone, and to go with the product to the Agriculture School where there was a polarimeter. He returned, very excited: the product exhibited rotation of polarized light! As we were readying a Communication on the extraordinary results, it occurred to us that the rotation might have been due to a residual amount of glucose, for which the sample tube had previously been used. And, indeed, when a properly washed tube was used, there was no rotation (and the

published result about the santonin synthesis was apocryphal). Carl's professor was not pleased, and suggested that Carl would be thrown out if he did further bootlegging chemistry.

The synthesis of the piperidine derivative, *cis*-3-ethyl-4-piperidineacetic acid, or 'cincholoipon', was my model goal for the *cis*-3-vinyl-4-piperidine acetic acid, or 'meroquinene', which I needed for a quinine synthesis based on previous work by the German chemist, Rabe. I am particularly proud of the way I made my starting material, *N*-benzoylaminodipropionic acid. This started by adding ethyl acrylate to ammonia until it was all converted to the tri adduct. Then I mixed it with benzoyl chloride, thus producing the *N*-benzoyl iminium salt, which on distillation decomposed to produce the wanted *N*-benzoyl-derivative of the di-adduct, after a forerun of ethyl acrylate. The synthesis also had an important feature: it was designed to give only the *cis* compound, and thus represented the first synthesis of a compound, related to a natural product, which was designed to give the correct stereochemistry. This was very significant because when the New York Times announced, about that time, that Woodward and Doering had synthesized quinine, meaning *cis*-3-vinyl-4-piperidinepropionic acid, 'homomeroquinene', their compound was accompanied by an equivalent amount of the *trans*-precursor. In other words, the W.-D. synthesis was entirely non-stereoselective. I remember that I called up Woodward, at Harvard, to ask him for the details of his synthesis, and that he was very willing to tell me. I later wrote him a letter, which he kept for some reason, in which I asked whether he or Doering tried to repeat the extraordinarily scanty reports of the German conversion of homomeroquinene to quinine (which I thought one needed to do to establish a 'synthesis' of quinine). But this remained unanswered.

My progress in the lab was only moderately affected by getting married to Winifred Stewart, the same young woman that I had met at St. Petersburg Junior College some years before. As I recall, I asked one of my lab partners to watch over a reaction while I went to meet my future wife in the office of the justice of the peace who was to marry us.

Shortly afterward, I became interested in the question of what I would do to get a job after my graduation with a Ph.D. Thesis in 1945. I was still on a visitor's (temporary) visa, which did not allow seeking full employment. Fortunately, things were not as rigid as they now are with the Immigration Naturalization Service (INS), and they somehow let me know that they would not do anything to prevent my getting a job, provided that I worked seriously on getting my status straightened out. And this is how it came about that, as a result of McElvain's efforts, I was hired by a little company in Milwaukee, Lakeside Laboratories, as 'Senior Research Chemist'. This was a remarkable achievement, until I realized that there were no other chemists, although there was a Director of Research and a dishwasher. In any case, I worked diligently on making thiophene analogs of simple benzene derivatives that were known to have useful pharmacological properties.

There was a rocking steel 'bomb' for hydrogenation as the one significant piece of equipment. I worked with it in the evening, when I conducted my own after hours experimentation. One really worthwhile thing I did was to find out that one could hydrogenate 2-methoxynaphthalene in the unsubstituted ring, giving 6-methoxytetralin. Simple oxidation gave 6-methoxy α -tetralone that became much more readily available than via the existing route from *m*-methoxyphenylbutyric acid, followed by Friedel-Crafts cyclization. 6-Methoxy- α -tetralone became the starting material for estrone and derived steroids, making me regret that I did not patent the reduction of 2-methoxynaphthalene.

William S. Johnson, whom I got to know when he was a young professor at Wisconsin, suggested that I apply for an independent research fellowship at Harvard. This I did, suggesting a synthesis of estrone, which had the merit of being stereospecific. Then one day the telephone on the concrete block wall rang. It was Professor Paul

Bartlett, the chairman of the Harvard Chemistry Department, who asked whether I would accept, instead of a Fellowship, an appointment as 'Instructor'. I immediately accepted, subject to my straightening out my visa problems.

And this is how my academic career started, as an Instructor (the lowest academic rank at the time). It was somewhat less than a year after the start of my job as an illegal alien at Lakeside Laboratories! I made a one day trip to Windsor, in Canada, to straighten out my status, becoming the proud possessor of an immigrant visa, which made it legal for me to get paid work.

In Cambridge, MA, the only place my wife and I could find to live was in a house at 25 Follen Street, which we shared with eleven other couples. It did have two bathrooms and two kitchens. I remember the many discussions on why we could not start a system for having the doors of the bathrooms fly open after 20 min. We had, however, complex systems for using the top of the stove while some other couple used the oven. Anyway, I somehow acquired a certain reputation as a stylist (maybe it was my accent), and knocks on our door were frequent, asking 'is Gilbert available?' for consultation about whether a certain dress would, or would not, look good.

It was when I first met R.B. Woodward who, at 28, was just five years older than me. He had not yet evolved his love of blue color and of 'old fashioned' drinks (these were before the daiquiris). He drove a strange contraption, an old Packard, that in addition to multicolor fixes of a variety of dents, had its right hand fender firmly attached to the body by copper wire. But it served to sometimes give me a ride back to 25 Follen Street in the evening. One of the first problems I got involved in came about in a peculiar way. After a seminar I had given on a possible synthesis of estrone, Woodward offered me an irresistible arrangement. He would give me half of three of his students, Aaron Nelson, Robert Wineman, and Aksel Bothner-By, if I would merge my plan to synthesize estrone with his view on how the C/D system could be made. I remember that the agreement was set in the Packard that had returned me to 25 Follen Street. We started work, and eventually a point was reached, toward the end of the synthesis, when a diacid, which only needed to be cyclized to give estrone methyl ether, was obtained. It had the same melting point as the diacid obtained by Miescher's group in Switzerland, in a less interesting and non-stereospecific synthesis. A very small amount of the correct Swiss diacid that was required for comparison with ours was obtained from Miescher. Woodward decided to take the melting point of this acid, mixed with our own, by himself. He had the melting point apparatus placed on a large white sheet on top of a laboratory bench, and prepared for the theatrical validation of our synthesis. At that point, bothered by all the pump and ceremonial, I went to Harvard square for a cup of coffee. When I returned, all was gloom in the Harvard labs. The 'mixed melting point' had been depressed by some 20°! It seems that the difficulty was that the Diels–Alder reaction had taken a totally unexpected course to produce a system different from what we had expected. It is interesting that Woodward removed all traces of that episode from the files he left for posterity.

At Harvard, I had a lab-office on the same floor as Woodward, with whom I usually had lunch when he was around, at a small coffee shop, Shrafft's, next to the Harvard Coop. I acquired some skill at explaining what might be in Woodward's mind, but was sometimes stumped, as when a beginning graduate student came in from a session with Woodward, wondering what was to be the next step with a Diels–Alder product he had made according to a previous request. 'Brominate it' had been Woodward's answer. I was unable to figure out what Woodward's further intentions might be.

I had to give a number of seminars at Harvard on topics that interested me, and on which I intended to work, but had not yet. They were very well attended by the likes of Fieser, Woodward,

Bartlett, and people from MIT, like Büchi, who filled the front row, while graduate students and postdocs filled the rest of the large lecture room, MB 23. On that particular day, my parents, who lived rather close to the chemistry building, had sneaked up to seats in the back of the room, unknown to me. They had come to hear their son, the great professor. I delivered my talk concerning some derivatives of morphine that I believed had been incorrectly formulated in the chemical literature. When I finished, waiting for the thunderous applause, which I anticipated, Louis Fieser arose from his place in the front row, his tall figure standing from the crowd. 'This is outrageous!' were the first words he uttered and continued 'you have the nerve to question the work of a major figure in morphine chemistry, without ever having had these compounds in your hands', he continued. My poor parents had really chosen the right seminar to attend!

I must say that Fieser had the courage to apologize after a few days, after he had time to look more seriously into the structures that had been assigned to the morphine derivatives. I was right, after all.

Harvard was also when I realized that I should wear glasses. This followed a lecture I had given, and had concluded by the question of whether anything I had lectured about had not been perfectly clear. I was told, by someone who sat in the back, that some twenty hands went up. 'Well', I said, 'if there are no questions, I'll see you next Tuesday.' That, plus the fact that Professor Bartlett had complained to Woodward that I did not acknowledge his greetings, convinced me to get glasses.

One of the students, who became a best friend, was Gurbaksh Singh, a graduate student of Woodward's. He was also a friend of one of my students, Albert Burgstahler who is the one who finished the synthesis of cantharidin in 1951. Burgstahler was very religious. He conceived the idea that if he could convert Singh to catholicism this would be a very notable accomplishment. And, indeed, it would have been, what with Sing's black beard and turban. Gurbaksh had expressed interest in this endeavor and, under Burgstahler guidance, started taking lessons that would eventually lead to his conversion. After several weeks, Burgstahler and Singh came to my office on the big day when conversion would take place, presumably to get my blessings for the event. I was completely favorable, and the two of them went to the priest who was to do the ceremony. After less than an hour, they came back, Burgstahler rather dejected. 'What happened?' I said. Well, Singh had no problem with all the details he had studied so carefully for weeks, but just before the conversion was to be finalized, Singh said 'There is only one thing; will this help my compounds crystallize?' When the priest could not guarantee this, all was finished. It is not known whether it was one of the longest shaggy dog stories, or whether it was a genuine concern.

Harvard was not all chemistry. On 'the trip' to California that we did with a second hand Mercury with Carl Djerassi and his first wife, I expressed no special desire for one itinerary over another, except that I needed to go through Las Vegas to test a foolproof system to make money at the roulette table. This was agreed upon and the big day in Las Vegas came. The 'system', I thought I had discovered, consisted of putting one dollar on red and, if it didn't win, doubling the amount to \$2.00 on red, then \$4.00, and so on. My wife, who did not like games of chance, left me early to go back to the motel where we stayed. I continued playing (using the money my wife had saved) until I had to put \$64 on red (having already lost \$63), or \$1020 in today's money. This took place so fast that I did not have time to change my money into casino chips. I remember the large amount of money on the table. The other customers held up playing to watch the obviously inexperienced gambler. When the little ball stopped in black, I felt that the croupier was stealing my money. I walked back to the motel. There, my wife was apparently asleep in the dark room. I pushed the door

open, not preventing an unwelcome squeaky noise. In the darkness, a voice could be heard: 'You lost it all, didn't you?'

As an Instructor, I obviously did ok in my teaching duties, which consisted mostly of supervising a course in qualitative organic analysis, and I was promoted two years later to Assistant Professor, a rank still without tenure, but which would allow me to get graduate students of my own, to work with me for their Ph.D.'s. They were outstanding: names like Burgstahler, van Tamelen, Conroy, Hill, were associated with my publications at the time. There were also several publications with the Syntex group in Mexico, for which I consulted. This consulting was arranged by Carl Djerassi who had become research manager at Syntex, a small drug company about to be heard of.

Syntex, at the time, was euphemistically called a pharmaceutical company. There were no hoods in the 'research' laboratories, operated mostly in the courtyard, where Mexican girls did their best to prepare progesterone from diosgenin. These were not easy times in Mexico, and thieves found it worthwhile to steal and sell even manholes covers. This led to a nearly disastrous result when, at night, a taxi carrying Carl Djerassi noticed another taxi carrying me in the opposite direction. Carl's taxi stopped to transfer him to my cab, but as luck would have it, by the side of a coverless manhole. Carl almost disappeared in it, but I just managed to grab his hand and to pull him back.

Probably my most important work in these Harvard years was the synthesis of cantharidin, which some have called the first of the planned stereospecific total syntheses of a natural product. And also my prediction that 1,5,9... polyenes would, if undergoing concerted cyclization, give trans-anti-trans six member rings, as one found in steroids and triterpenes. This concept was later called the Stork–Eschenmoser hypothesis, and became the basis for the beautiful work of W.S. Johnson on the synthesis of steroids and triterpenes.

Anyway, it became clear that Harvard would not grant me tenure (the chairman of the department, George Kistiakowsky, greeted my being half an hour late in turning over a Ph.D. thesis to his office by 'I wish I was in the old Russia, so I could have you strangled during the night'). So, in 1952, I started thinking of other places to go. Professor John D. Roberts, whom I had met at Harvard when he was an independent postdoctoral fellow, recommended to Professor Louis Hammett of Columbia University that he should add me as a tenured Associate Professor there. After a visit, which included a lecture on my anticipated work, I was selected to become an Associate Professor at Columbia. I still remember that I arrived in New York in February 1953, having bought a house in the New Jersey town of Leonia, just minutes from Columbia University. That little town of around 7000 people was a very convenient place to live with a growing family. It had reasonably good schools and had been a favorite of many earlier members of the Columbia family, including Enrico Fermi of atomic energy fame, and Harold Urey, the discoverer of deuterium.

We can be impressed by the inflation that eventually took place when I reveal that the house that I acquired cost me all of twenty thousand dollars! Most houses in Leonia were on very small plots of land, without fences and close enough to the neighbors that one could almost touch hands with them through the windows of the second floor. But it was nice and comfortable. In general, it was the kind of neighborhood where one did not lock one's door at night, and just walked over to a neighbor to get some needed sugar or coffee. We had two more children there, Janet and Philip, making it a total of four with our two previous ones, Diana and Linda, from Cambridge. Raising the children was totally left to my wife, but I do remember a small contribution I made. It had been decided that I would be in charge of bottle-feeding in the middle of the night. I did this pretty successfully, but I found it quite slow and time consuming. This is where I made an improvement, which was

extremely simple, and, which I now can reveal: I simply enlarged the size of the pinhole in the rubber nipple. The result was as expected, with only a small amount of milk wasted, when the baby could not handle the flow of milk.

The organic chemistry group at Columbia had become a disaster. Its 'names', Robert Elderfield, David Curtin, and William Doering had all left, simultaneously, in the belief that the other two would stay. There was only one tenured professor, Cheves Walling, who had come to Columbia six months before me, after making a name for himself in free radical chemistry.

I had some influence in rebuilding the department. First, there was Ronald Breslow whom I had known as an extremely bright undergraduate at Harvard, where he worked with Woodward, and who was about to terminate a postdoctoral with Alexander Todd in Cambridge, England. I offered him a job. The telegram he sent accepting it was opened by Louis Hammett, the chairman of the department, at the start of a department meeting. 'What does this mean', said Hammett, the department has not even voted on this'. 'Oh, that's just a code. It means that he would accept, if we made him an offer.' Then, Nick Turro, who was strongly brought to my attention by John D. Roberts, and became really attractive when he told a long and complicated joke during his lecture. The self confidence it implied, together with his many other accomplishments, made certain an offer of a Columbia job. Thomas Katz was appointed when Breslow and I concluded that he did not intend to work on what he told us, but was smart enough to do important things. And Koji Nakanishi, whom I had known as a Fieser postdoctoral associate at Harvard, and was too polite to ask for time to think about our offer that he leave Japan and come to New York. Columbia became again a great organic chemistry department. It continued in that position with the appointments of Samuel Danishefsky and of Clark Still, two former postdoctorals of mine. It has been a source of considerable pride that no one who joined the Columbia department with tenure in organic chemistry since 1954 left for another university, in spite of many opportunities.

My office at Columbia was rudimentary. It would not have been possible to have more than two people in that room, which also had a couple of files, a desk, and a blackboard. But this was actually sufficient for my normal dealings with the research students who were almost all on the same (sixth) floor of Chandler. The intellectual potential of that little room was quite enhanced by the visit of Linus Pauling who had come to try to convince me to move to Cal Tech where he had become chairman of the Chemistry Department. I was quite impressed, and I took Pauling for lunch to the Faculty Club, the usual place where most of the Chemistry Department members ate, all at a large table in the middle of the room. I chose a spot that was isolated, but quite visible, and enjoyed the anticipated puzzlement of the Columbia chemists wondering what Pauling would have in common with Stork to visit him at Columbia. Incidentally, I proceeded quite rationally to decide on the pros and cons of Cal Tech versus Columbia: I made lists of the relative advantages of the two places. Any time Cal Tech edged forward, I modified the value given to one or the other items, in favor of Columbia. I stayed at Columbia.

Things went forward more or less normally in New York, but one event I remember was the launching of *Tetrahedron*. Captain Maxwell, as the editor of the journal in question was known, had invited in April 1957, a number of guests in a townhouse in downtown New York to mark that event. During the celebrations, Maxwell placed a bet with some of the guests, namely Bob Woodward, Bill Doering, Carl Djerassi, and myself that the circulation of *Tetrahedron* 'will not exceed 2499 copies' by April 24, 1961 (See Fig. 1). The bet, which was witnessed by Sir Robert Robinson, was for 100 gold guineas. This was a clever bet, because Maxwell would essentially get four salesmen for his new journal in exchange for a relatively small amount of money. Time passed, and one day I

Capt. J.R. Dawson places with
 the venerable red gentleman the
 wager, in the amount 100
 gold guineas, in respect to
 each gentleman signing, that
 the circulation of TETRAHEDRON,
 assuming continuous publications
 throughout the relevant period,
 will not exceed 3499 copies
 by 24. IV. 1961.

W. J. J. J.
 W. J. J. J.
 Gilbert Stork

The above represents a true statement
 of fact.
 Maxwell

Witness:

Robert Robinson

Fig. 1. A clever wager for Robert Maxwell.

received a phone call from Woodward who said 'you know, we won the bet'. I did not know, but I eventually got a call from Maxwell who suggested I meet him in a townhouse downtown where, after some champagne, he gave me a copy of a letter from a bank in Basel stating that 100 gold sovereigns (the bet had been changed to sovereigns by mutual agreement) was waiting for me in the branch of the Swiss bank in New York. I went there, carrying a French newspaper that I thought would give me some appearance of respectability, and was introduced to a vice president who did, in fact, hand me a small bag containing 100 gold sovereigns. This, after many years, is worth quite a bit. In 2011, at the time of this writing, 100 gold sovereigns equal in excess of \$30,000!

Columbia years were also marked by car stories, of which I will tell just a few. I bought a Fiat 600 that I arranged to purchase in the U.S. and was to pick it up in Milan, during a summer trip. When we got to Milan, finding the garage where it was kept turned out to be more difficult than expected. This was possibly, in part, because of an agreement between Fiat and American companies that they would not export Fiats, at least the 600, for some time. The address listed on the car's documents was, therefore, Gilbert Stork, Baghdad... We got this car back to the U.S. where it proved extremely convenient: it was small enough (about 3 feet shorter than a Volkswagen) that it could get in anywhere, sometimes too easily. I recall once leaving the chemistry building as three of my graduate students, Dave Goldsmith, Bill Reusch, and Bob Augustine, were carrying the car and trying to get it in the building's elevator to deposit it somewhere. This car was, unfortunately, not serviced properly and could finally only be driven on level ground. It ended

when I took it to a gas station—without any hill to negotiate—and inquired about selling it. 'I would be able to offer you so little, you wouldn't want to sell it' 'Try it', I said. '10 dollars', he said. 'That's yours', I said.

After that, I went to see a green Austin that was advertised in a local paper. For some reason, it appeared attractive to me, and I bought it even before we reached it. I then discovered that it had to be towed by the sellers to get to my home. 'Get them to take it back, even if you have to pay them' was my mechanic's advice. But perhaps the most peculiar of my car stories involved a white Simca, with red interior, which I purchased in France, perhaps because it looked so good driven in a movie (it's true that Brigitte Bardot was the driver). Coming back in that car from some lectures I had given at Yale, the motor exploded on the parkway. I had enough of it, and decided to abandon it. I was proceeding with removing its license plates when a police car showed up. Its occupant asked what I was doing. I explained, but a better idea crossed my mind. Actually I said, 'I'm going to give it to you, if you can take me home'. 'I can't do that' he said, not with a car marked 'Connecticut Police' 'All right, you take me to the Hartford train station where I can take a train to New York. I will actually charge you \$25, so there will be some evidence that the car is no longer mine.' This transaction was carried out. When I called my wife for a ride from New York to our New Jersey home, she asked 'what happened to your car?' 'I sold it to a policeman' was my answer.

One of my 'Car Stories' could have had a bad ending. That evening I had parked my car on the street just by Columbia. When I returned, everything seemed normal, and I took off for New Jersey in the second hand Jaguar I was fantasizing with at the time. Approaching the George Washington Bridge, I could feel a certain floating in the car's ride, suggesting a possible flat tire. This led me to drive cautiously on the extreme right, but all of a sudden the car leaned to its side in a shower of sparks. These came from brake drum scraping the roadway, and simultaneously there was my entire left front wheel rolling away. It was night, and I could not see what happened to the wheel. At this time a police car appeared, and I was placed in it while they investigated. The police radio was on, and at first its message did not seem especially relevant until 'another one has got hit' suggested that my wheel was alive and active.

There was at that time no concrete separation between the lanes going to New Jersey and those going to New York. It was eventually pieced together that the wheel had crossed over to the New York bound lanes and ripped off the right fender of a car, being sent back to the New Jersey lanes where it apparently ripped off the rear view mirror of another car, sending it through the windshield of another, and finally bouncing off its hood and ending the mayhem by plunging in the Hudson River, quite some feet below. The wheel was never found. Miraculously, there were no more than a few cuts. The car was eventually repaired, and met Professor D.H.R. Barton's security inspection before he entered it, after it re-entered service.

I will end these sad stories with one in which a car is but indirectly involved. It was winter, and I had taken my children 'skiing' in New Jersey on a Sunday around noon, and I was probably driving some ten miles over the limit, with no other car in sight. I was stopped by a policeman, who issued a ticket requiring that I go to Court. I went on the appointed date. I was shocked that the old judge asked for my driver's license, and put it in an envelope, which he sealed. 'What are you doing?' I inquired. 'Well, you will get it back in a month' said the judge. Apparently, the law at the time was that going ten miles over the speed limit was punished by loss of the driver's license for a month! I was furious, and drove back home without a license. The next day, it seemed that I had promised my oldest daughter, Diana, to drive her to Manhattan on a shopping expedition. I tested the water at dinner 'What would you do if your father had his driver's license suspended for a month?' 'I would leave home' said Linda.

I couldn't take that chance. I felt I would have to take Diana to Manhattan the next day, driver's license or no driver's license. This turned out ok, but when my wife asked my daughter how the trip went, the answer was 'It was fine, but at almost every intersection I don't know why daddy asked me to look out the back window whether I could see a policeman'.

Life went on in Leonia, with the usual schoolwork for the children, but I remember a story in which Diana had a bad cold so she was kept in her second floor room, overlooking the back yard. In the garden, a neighbor's child was pulling the wings off some insect. 'You should not do that' said one of the other neighbor's children, 'They are all God's creatures'. That's all right was the advice from the second floor window: 'We do not believe in God in this family'.

At the laboratory, things were also normal, but I remember a seminar where, as usual, we had brought our lunch that, in my case, consisted of a sandwich of roast beef. One of my students rushed in, claiming that there was a phone call for me outside. While I was gone, they replaced the roast beef in my sandwich by an embalmed large frog, acquired from the biology course one of them was taking. When I returned, I could see what they had done because the frog's little legs were showing out of a side of the sandwich. I would take the sandwich and, looking as if I was going to take a bite of it, I would interrupt the motion and ask a chemical question. This went on a few times until they admitted their evil deed. Actually, the wife of Roy Rubin, one of the perpetrators, made a model of a large frog getting ready to eat a sandwich of people, and gave it to me. I still have it in on the top of the drawer in my bedroom.

The rest of my life has been well documented. A number of awards have come my way. When I was elected a member of the National Academy of Sciences I was only thirty nine, and I had only a vague inkling of the existence of that institution. It was a Leonia neighbor, not a chemist, who called from Washington to tell me they had read in the paper the news of my election. All I can say is that it is amazing how much more difficult it is to be elected today.

Another award that made quite an impression on me was my receipt of the National Medal of Science. My wife and I were vacationing in the U.K. and were visiting friends, when the telephone rang and, improbably, 'it's for you' followed. The person on the phone stated that this was the White House calling. I could only think of the White House Hamburger chain and it took a little while to straighten things out. But they were straightened out, and I received the medal in the White House, from President Reagan.

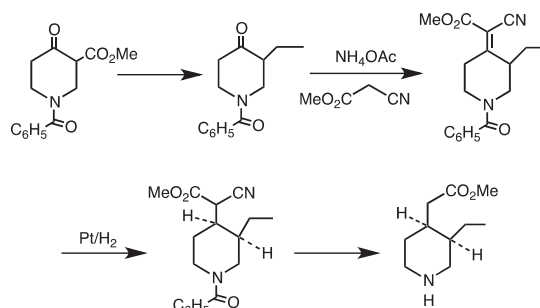
I eventually had to retire in 1992 when I became 70 years old. This was almost the year that retirement was no longer mandatory, but that was also the occasion for an extraordinary event, my retirement celebration. A symposium was organized by Clark Still and Ayako Yamashita to commemorate the occasion, during which lectures were given by some of my former associates. I still have the photograph of the many graduate students and postdocs who came back for the occasion: almost 250 of my former associates in front of the large statue of Alma Mater at Columbia. Nearly 400 people, including spouses, attended the dinner party on a boat that sailed the Hudson in the evening. And Paul Grieco announced that donations, solely by my former associates, would endow an annual lecture, the Stork Lecture, which continues to this day. A memorable way to retire.

2. Part 2. Chemical retrospective. Reactions we introduced

2.1. Stereocontrolled syntheses

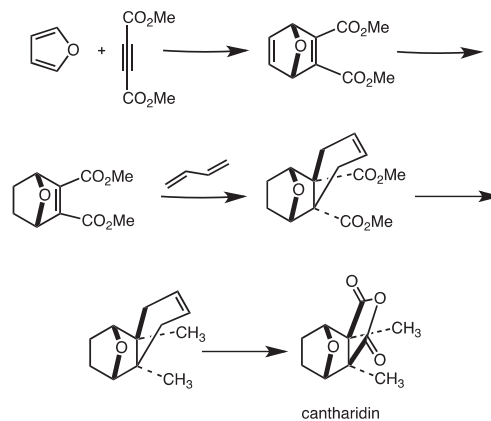
I start by pointing out that, when I started in chemistry, stereochemical planning was not a concern of synthetic chemists. The first work I did was to synthesize cincholoipon, *cis*-3-ethyl-4-piperidineacetic acid, which I thought a useful compound as

model for a quinine synthesis. Since that compound was *cis*, I devised a method that would—and did—give the *cis* compound exclusively (Scheme 1).¹



Scheme 1.

I believe that this was one of the first planned stereocontrolled synthesis. It was followed, after I moved to Harvard, by the synthesis of cantharidin that was achieved via a couple of Diels–Alder reactions. I remember very clearly that Albert Burgstahler, who finished the synthesis around 4 am, went to the roof of the building every so often to sing Gregorian chants, to help the crystallization of the final product—cantharidin. Whether this helped cannot be ascertained, but cantharidin did crystallize. I recall that I left around 4 am to go to the airport to catch a 7 o'clock plane to Mexico, where I was due to consult at Syntex (Scheme 2).



Scheme 2.

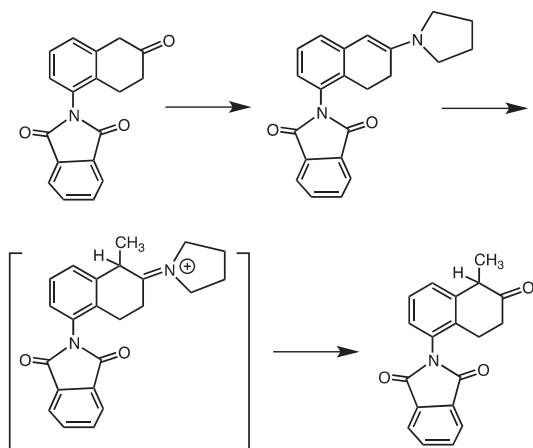
2.2. Cantharidin

This was probably the first natural product synthesized stereospecifically.² It was not, however, in the same league as Sarett's synthesis of cortisone, submitted a little over a year later, which was the first synthesis of a *complex* natural product accomplished stereoselectively.

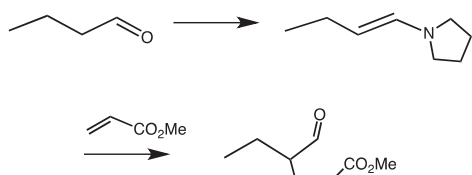
2.3. Enamine alkylation

The enamine alkylation^{3,4} was conceived with no help from biochemistry. It is true that the mechanism of action of one class of aldolases is now known to proceed via enamines, but as late as 1955, a year after our first enamine paper, the biomechanism of aldol formation was still not clear.⁵ It is very interesting that proline has proved to be a very successful base with which to produce chirality in enamine alkylation, and it is, of course, a pyrrolidine. I had been wondering how Nature managed to do aldol condensations, and I suggested to Ross Terrell, a graduate student in another group, that he try the pyrrolidine enamine of his ketone, 5-phthalimido-2-tetralone, to see whether one could avoid the

dimethylation, which resulted under standard conditions, using a sodium enolate. This was particularly lucky because 2-tetralones, in general, make the best subjects for enamine alkylation with methyl iodide. Mono methylation is obtained in ~80% yield! Most alkylations are not so satisfactory, and usually only reactive halides, such as alkyl and benzyl halides, or α -bromocarbonyl compounds, give satisfactory yields. Michael components, such as methyl vinyl ketone or alkyl acrylates, are different in that they give excellent yields, even with α -unsubstituted aldehydes (Schemes 3 and 4).

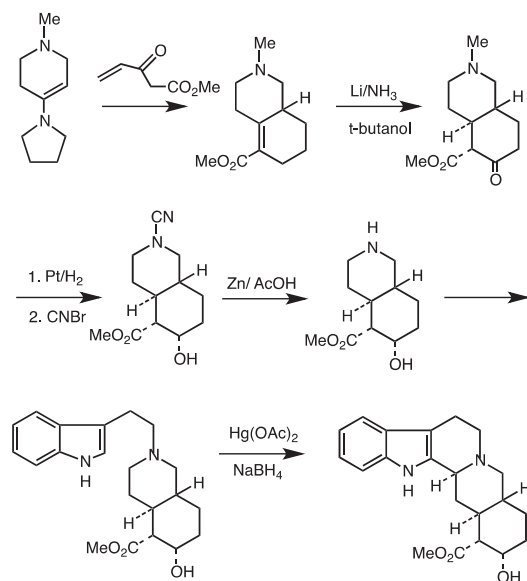


Scheme 3.



Scheme 4.

An example of the use of enamines in the total synthesis of natural products is the synthesis of yohimbine (Scheme 5):⁶



Scheme 5.

The considerable extension of the use of enamines to the catalytic conversion of aldehydes and ketones to aldols is a recent

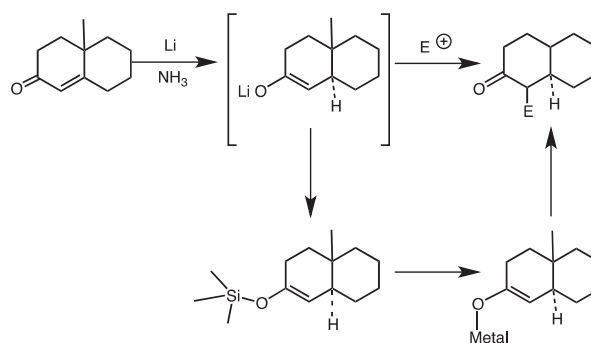
development that extends the range of the 'enolates without metal' of enamine chemistry (organocatalysis).

2.4. Alkylation with anions of imines

The alkylation of enamines with alkyl halides is only exceptionally a good reaction (with 2-tetralones, for instance). In order to get around this difficulty, we introduced the alkylation of imines.⁷ These were deprotonated originally with ethyl magnesiumbromide, but eventually lithium diisopropylamide was used. The metalloenamine alkylation was completely general and gave only monoalkylation, reflecting the slow formation of enamine anions. It could be used with aldehydes, as well as ketones, and with fairly unreactive halides, such as β -haloacetals and ketals.

2.5. Regiospecific enolates. Formation and trapping

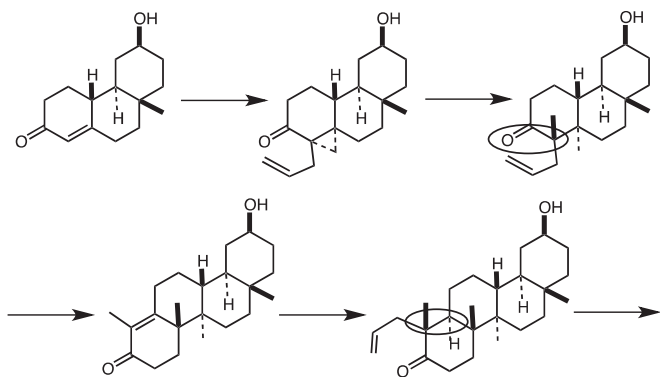
The specific formation of one of the two possible enolates from an unsymmetrical ketone was a difficult problem. A solution, in some cases, had been the use of a 'blocking group', a substitution, which would block enolization on the favored side of the ketone, and could be removed after its purpose had been served. At the very best this procedure, contributed to by, such as Robinson, Johnson, Ireland, and Woodward, cost two additional steps. We thought that in the Birch reduction of conjugated ketones, the product must be the enolate ion rather than the saturated ketone. If that was the case, then it might be possible to use this enolate before working up the solution, and the problem would be solved. Unfortunately, the sodium, or potassium, enolate equilibrated during alkylation. We thought that the lithium enolate would possibly survive long enough for alkylation, and this proved correct:^{8,9} lithium/ammonia reduction of α,β -unsaturated enones gave an enolate ion, which could be alkylated in the ammonia solution. It could also be isolated as its trimethylsilyl enol ether.^{10,11} This allowed its NMR to be checked, and the enol ether could later be converted, in any solvent, such as THF, and with any organometallic species, to give any desired metal enolate, free of unwanted material (Scheme 6).



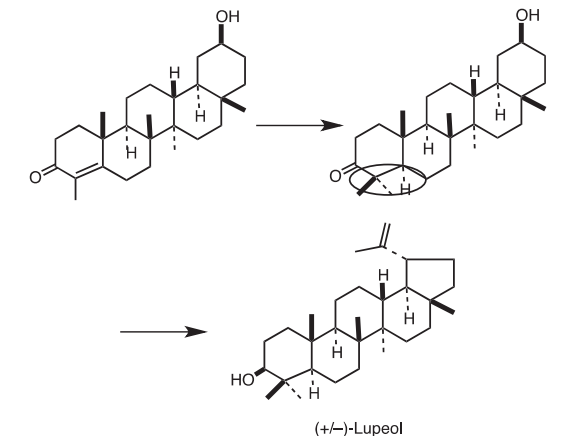
Scheme 6.

The synthesis of lupeol¹² is a good illustration of the power of regiospecific enolate synthesis and trapping: it is used three different times in that total synthesis (marked by a lasso symbol) (Scheme 7):

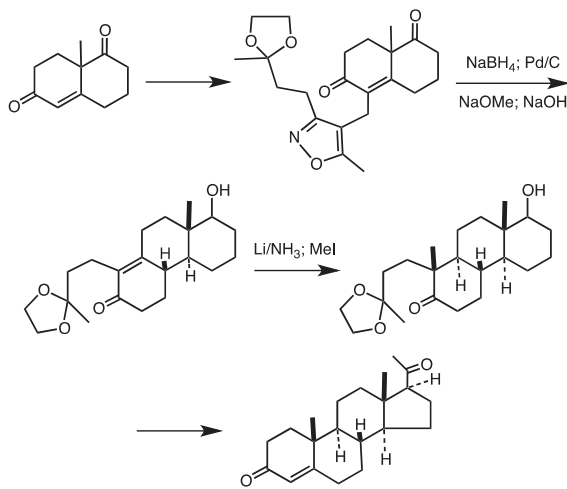
Perhaps this is the place to mention some of the considerable amount of work we did on finding a substitute for vinyl ketones that would be compatible with regiospecifically formed enolate ions. I will restrict myself to isoxazole chemistry in a synthesis of progesterone (Scheme 8):^{13,14}



Scheme 7.



Scheme 8.



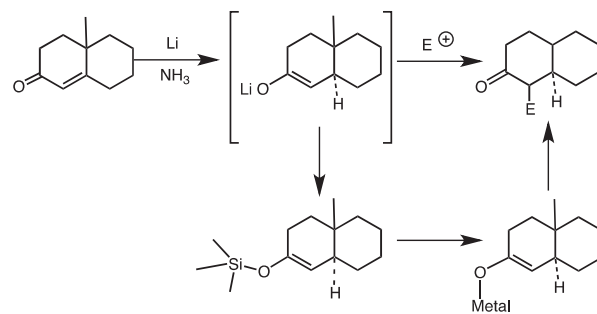
Scheme 9.

We eventually realized that the addition of cuprates to enones would also produce regioselective enolates.¹⁵ These could be used directly with sufficiently reactive species, such as cyanofornates¹⁶ or trifluoroethyl formates,¹⁷ or they could be taken through the silyl enol ether, and subsequently converted into the lithium (or other) enolate (Scheme 9).

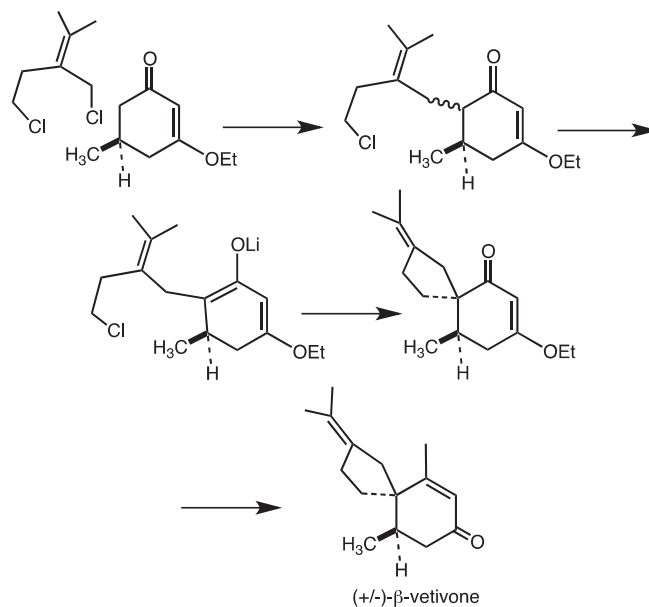
While on the subject of carbonyl enolates, I might mention the kinetic formation of enolates from enol ethers of β -diketones that was used in a very simple synthesis of β -vetivone (Scheme 10).¹⁸

2.6. Intramolecular addition of unsaturated diazo ketones

It was well known that diazo ketones from acids are transformed, e.g., by silver ion (Wolf rearrangement), to homologous

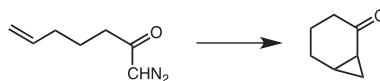


Scheme 10.



Scheme 11.

carboxylic acids or their derivatives. This is, of course, the second step of the Arndt–Eistert sequence for the homologation of acids. It seemed possible that, if an olefin was present, addition could precede rearrangement and lead to insertion into the olefin. This possibility was explored by Jacqueline Ficini, then a postdoctoral from Paris. The reaction took place, as had been hoped, to give the desired product, after heating in the presence of finely divided copper.¹⁹ The reaction is now usually done with rhodium rather than copper, and has proved very general (*Organic Reactions* Vol. 26 had already 230 references in 1979) (Scheme 11).

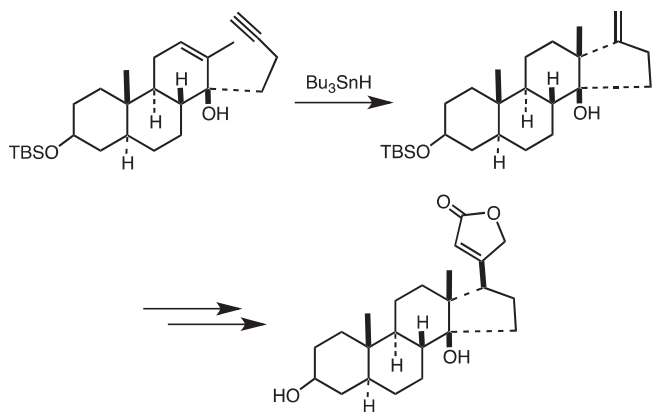


Scheme 11.

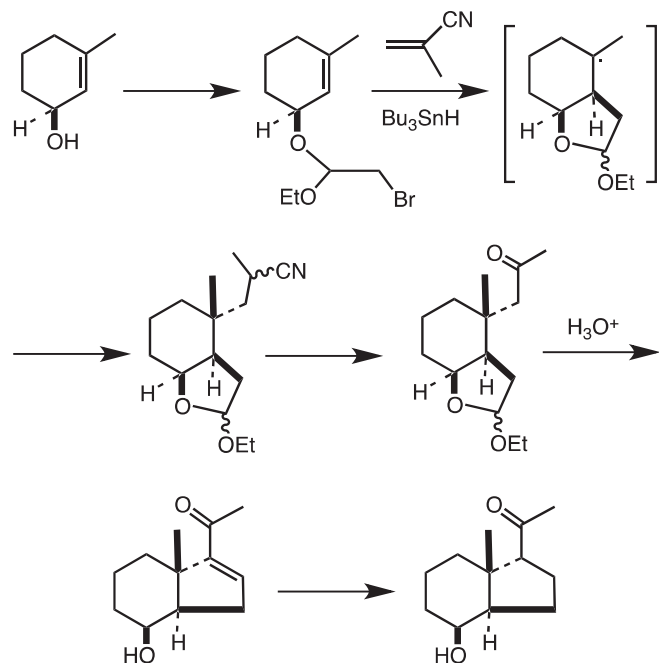
This was also my last attempt at doing something useful in the laboratory. To prove the structure of the compound we had synthesized, it seemed simple to make it from *m*-hydroxybenzoic acid. I claimed that the seven trivial steps this would require could be easily done in a couple of days. This caused Jacqueline Ficini, and Frances Hoffman (a long time collaborator of mine) to bet me \$50 each that I could not do it in two days, starting at 9 am, and stopping at 7 pm. The 2,4-dinitrophenylhydrazones of the final ketone would also have to return a satisfactory analysis. I won that bet (which, incidentally, would now be worth more than \$500). Obviously, their confidence was based on their observation of some previous attempts at my working in the lab.

2.7. Free radicals in the control of regio- and stereochemistry

More recently there were various contributions to the use of radicals in organic synthesis. We were the first to use vinyl radicals in synthesis²⁰ and formed them either from vinyl bromides or by addition of Bu_3SnH to acetylenes.²¹ We used them in the synthesis of (+) digitoxigenin (Scheme 12).²²

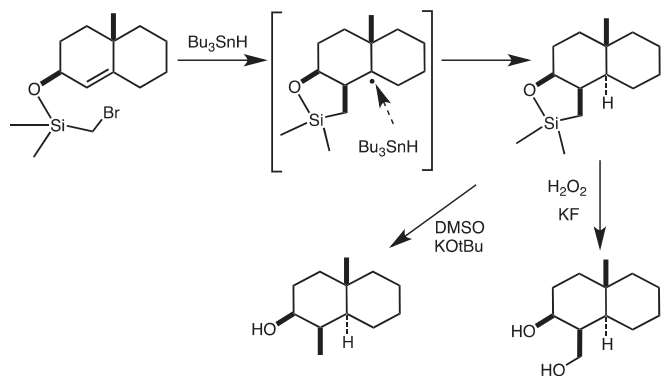


Scheme 12.

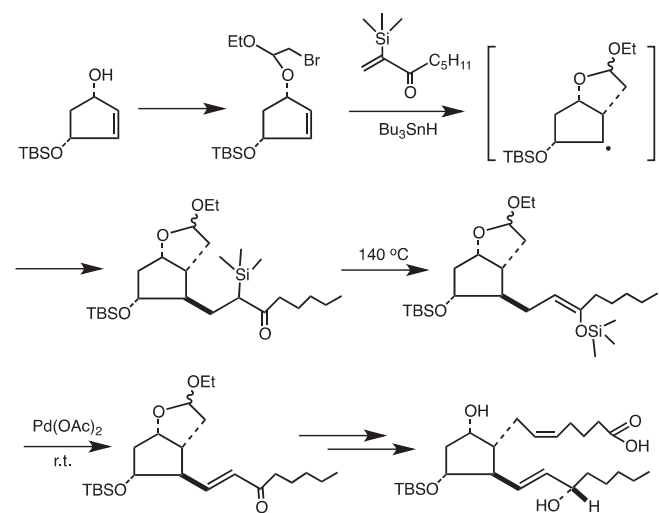


Scheme 14.

We also devised what we called the ‘temporary silicon connection’ to attach precursors of either hydroxymethyl or methyl. This may have been the first use of the temporary silicon connection to produce not only vicinal stereochemical control but, in selected situations, ring junction stereochemistry as well (Scheme 13).^{23,24}



Scheme 13.

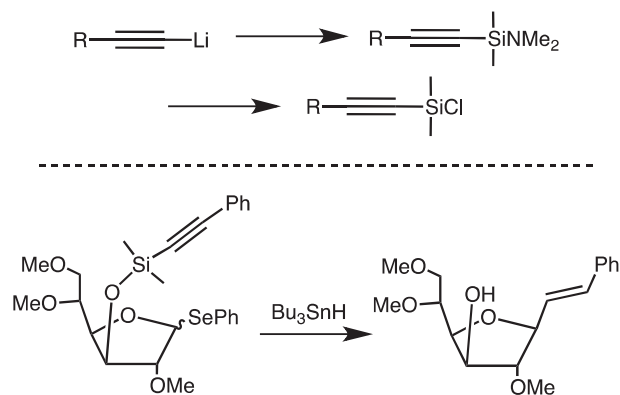


Scheme 15.

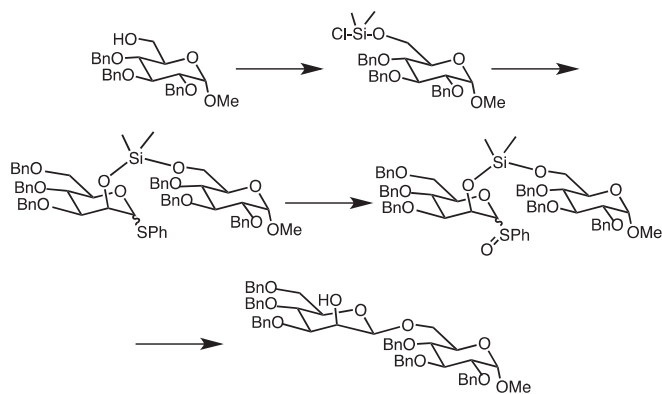
The connection was not always temporary, as with the bromoacetal connection, which served to control the stereochemistry of an acetaldehyde unit introduced into an allyl alcohol. The two examples, which follow show this, as well as the trapping of the first radical formed. They show very simple syntheses of a CD ring on the way to vitamin D,²⁵ and of a prostaglandin.²⁶ They illustrate the use of the Ueno–Stork reaction (a review in 2004 already had 239 references) (Schemes 14 and 15).²⁷

Other examples of the silicon connection to control reactions involved a radical in the *acceptor*, as in the synthesis of C-styryl glycosides of predictable stereochemistry (Scheme 16):^{28,29}

In a context not involving radical chemistry, the temporary silicon connection could also be used, for instance, to make



Scheme 16.



Scheme 17.

disaccharides in which the stereochemistry of the glycoside link is determined by attachment to a hydroxyl group near the anomeric center (Scheme 17).^{30,31}

Acknowledgements

My deepest thanks are due to all the members of my group, undergraduates, graduate students and postdoctoral associates who have used their talents to create the work for which we are known. Only a few are mentioned in the small bibliography that follows, but, to all of them, thank you.

References and notes

1. Stork, G.; McElvain, S. M. *J. Am. Chem. Soc.* **1946**, *68*, 1049.
2. Stork, G.; van Tamelen, E. E.; Friedman, L. J.; Burgstahler, A. W. *J. Am. Chem. Soc.* **1951**, *73*, 4501.
3. Stork, G.; Terrell, R.; Szumskovicz, J. *J. Am. Chem. Soc.* **1954**, *76*, 2029.
4. Stork, G.; Brizzolara, A.; Landesman, H.; Szumskovicz, J.; Terrell, R. *J. Am. Chem. Soc.* **1963**, *85*, 207.
5. Rose, I. M.; Rieder, S. V. *J. Am. Chem. Soc.* **1955**, *77*, 5764.
6. Stork, G.; Guthikonda, R. N. *J. Am. Chem. Soc.* **1972**, *94*, 5109.
7. Stork, G.; Dowd, S. J. *J. Am. Chem. Soc.* **1963**, *85*, 2178.
8. Stork, G.; Rosen, P.; Goldman, N. L. *J. Am. Chem. Soc.* **1961**, *83*, 2965.
9. Stork, G.; Rosen, P.; Goldman, N.; Coombs, R. V.; Tsuji, J. *J. Am. Chem. Soc.* **1965**, *87*, 275.
10. Stork, G.; Hudrlik, P. F. *J. Am. Chem. Soc.* **1968**, *90*, 4462.
11. Stork, G.; Hudrlik, P. F. *J. Am. Chem. Soc.* **1968**, *90*, 4464.
12. Stork, G.; Uyeo, S.; Wakamatsu, T.; Grieco, P. A.; Labovitz, J. *J. Am. Chem. Soc.* **1971**, *93*, 494.
13. Stork, G.; Danishefsky, S.; Ohashi, M. *J. Am. Chem. Soc.* **1967**, *89*, 5459.
14. Stork, G.; McMurry, J. E. *J. Am. Chem. Soc.* **1967**, *89*, 5464.
15. Stork, G. *Pure Appl. Chem.* **1968**, *17*, 383.
16. Mander, L. N.; Sathi, S. P. *Tetrahedron Lett.* **1983**, *24*, 5425.
17. Zaya, G. H. *Org. Lett.* **1999**, *1*, 989.
18. Stork, G.; Danheiser, R. L.; Ganem, B. *J. Am. Chem. Soc.* **1973**, *95*, 3414.
19. Stork, G.; Ficini, J. *J. Am. Chem. Soc.* **1961**, *83*, 4678.
20. Stork, G.; Baine, N. H. *J. Am. Chem. Soc.* **1982**, *104*, 2321.
21. Stork, G.; Mook, R. J. *J. Am. Chem. Soc.* **1987**, *109*, 2829.
22. Stork, G.; West, F.; Lee, H. Y.; Isaacs, R. C. A.; Manabe, S. *J. Am. Chem. Soc.* **1996**, *118*, 10660.
23. Stork, G.; Kahn, M. *J. Am. Chem. Soc.* **1985**, *107*, 500.
24. Stork, G.; Sofia, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 6826.
25. Stork, G.; Hutchinson, D.; Okabe, M.; Parker, D.; Ra, C. S.; Ribereau, F.; Suzuki, T.; Zebovitz, T. *Pure Appl. Chem.* **1992**, *64*, 1809.
26. Stork, G.; Sher, P. M.; Chen, H. L. *J. Am. Chem. Soc.* **1986**, *108*, 6384.
27. Solom-Roig, X. J.; Dennis, F.; Renand, P. *Synthesis* **2004**, 1903.
28. Stork, G.; Keitz, P. F. *Tetrahedron Lett.* **1989**, *30*, 3981.
29. Stork, G.; Suh, H. S.; Kim, G. *J. Am. Chem. Soc.* **1991**, *113*, 7054.
30. Stork, G.; Kim, G. *J. Am. Chem. Soc.* **1992**, *114*, 1087.
31. For a review of related work on the temporary silicon connection, see Abstracts of 32nd National Organic Symposium, Organic Chemistry Division, ACS, 1991; p 115.