



Dawn of organopalladium chemistry in the early 1960s and a retrospective overview of the research on palladium-catalyzed reactions



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Contents

1. Prologue	6331
2. Initiation of research on organopalladium chemistry	6332
3. Discoveries of carbonylation reactions and carbon–carbon bond forming reactions mediated or catalyzed by either Pd(II) or Pd(0)	6332
3.1. Carbonylations and decarbonylations	6332
3.2. Reaction of cyclooctadiene with malonate	6335
3.3. The birth of π -allylpalladium chemistry	6335
4. Beginning of the golden age of organopalladium chemistry	6336
5. Palladium-catalyzed reactions of various allylic esters via π -allylpalladium complexes under neutral conditions; facile decarboxylation is the key step	6337
5.1. Reactions of allyl carbonates	6337
5.2. Reactions of allyl β -keto carboxylates and related compounds	6337
5.2.1. Introduction	6337
5.2.2. Allylation by reductive elimination	6338
5.2.3. Preparation of α,β -unsaturated carbonyl compounds by β -hydrogen elimination	6339
5.2.4. Synthesis of α -methylene carbonyl compounds by deacetoxylation	6339
5.2.5. Removal of the ester groups from substituted β -keto esters and malonates by hydrogenolysis using formates	6339
5.2.6. Palladium-catalyzed aldol condensation	6340
5.2.7. Palladium-catalyzed Michael addition	6341
5.2.8. Conclusion	6341
5.3. Palladium-catalyzed hydrogenolysis of allylic compounds	6342
5.3.1. Introduction	6342
5.3.2. Control of regioselectivity in the hydrogenolysis of allylic compounds	6343
5.3.3. Preparation of exomethylene compounds	6344
5.3.4. Regio- and stereoselective generation of cis and trans ring junctions in decalin systems	6345
5.3.5. Stereocontrolled construction of the C-20 configuration in steroid side chains	6346

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6. Epilogue	6346
Acknowledgements	6346
References and notes	6346
Biographical sketch	6348

1. Prologue

I was born in 1927 in the small town of Oumihachiman near lake Biwa, which is the largest lake in Japan. When I was a boy, I enjoyed fishing and swimming in lake Biwa. After finishing primary school, I entered the commercial school in town, which is one of the oldest commercial schools in all of Japan. This does not mean that I was interested in studying commerce, but simply, there was no alternative at that time. What I learned in the commercial school became obsolete and useless in my life except for the use of the abacus, which is called 'soroban' in Japanese. Through use of the abacus, I became an expert at quick mental calculation, which has proven helpful in my research. After graduation from the commercial school, I changed my course of study and enrolled in Hikone Technical College, where I began to study chemistry. Fortunately I was taught by a very good teacher and became deeply interested in the subject. In order to continue my studies, I entered the chemistry department of Kyoto University in 1948. Frankly, I was disappointed. It had been three years since the end of the war, and there was no atmosphere of active research due to a serious shortage of equipment, reagents, and even food. When I graduated from the university, Japanese industries were extremely depressed and it was difficult to find a good job, so I spent a few years in a laboratory of a rather small pharmaceutical company in Kyoto.

Several years later, I was determined to go to the US to study chemistry further and applied for the Fulbright fellowship. Thanks to the Fulbright travel grant, I had the opportunity to go to the US in 1956, spending one year at Baylor University in Texas while completing an MS degree with honors. I then sought to enter graduate school and sent applications to MIT, Columbia University and the University of Illinois. I was only accepted at Columbia.

I enrolled at Columbia and began my graduate studies in organic chemistry, majoring in natural product synthesis under the guidance of Professor G. Stork. He was not only well-known for his elegant total syntheses of complex molecules of natural products but also a gifted teacher. Because he didn't have a secretary, the door of his office on the sixth floor of Havemeyer Hall was always open, and we could enter anytime without appointment to ask his advice about our problems and questions, to which he gave pertinent answers. Professor Stork received the Tetrahedron Prize in 1985 and wrote the article 'Chemical Reminiscences'¹ in *Tetrahedron*, which is exceptionally lengthy. He usually wrote rather short articles. At that time, R. Breslow was a young and active associate professor in the same department, and the Stork and Breslow groups held a joint seminar every Thursday night to mainly discuss reaction mechanisms, which was very instructive for me.

I worked hard for three years on natural product synthesis and received my Ph.D. degree in 1960. The title of my thesis was 'Studies toward the total synthesis of vitamin D and synthetic studies related to the Aconite-Garrya alkaloids'. Three years was the shortest on record in the Department of Chemistry at Columbia. Usually, it takes four or five years. Stork published one joint paper with me.² In retrospect, I should say that Columbia gave me the greatest chemical education of my life. I learned that the most important and eternal problem to be investigated in organic synthesis is the discovery and development of new methods for carbon-carbon bond formation.

After finishing graduate work, I returned to Japan and initiated my independent research career in 1962 at the Basic Research Laboratories of Toray Industries Inc. in Kamakura. Toray is the largest producer of synthetic fibers in Japan. I became convinced that I should discontinue work on natural product synthesis, which I learned at Columbia, and instead I selected organopalladium chemistry to be my research topic. Dr. T. Hoshino, Emeritus Professor at the Tokyo Institute of Technology and the Director of the Basic Research Laboratories, emphasized freedom of research, encouraging researchers to select their own research topics. I will try to explain why and how I began researching organopalladium chemistry at Toray.

The progress in synthetic organic chemistry has been remarkably accelerated since the 1970s. This is particularly due to the application of transition metal catalyses. Presently, research on 'Organometallic Chemistry directed toward Organic Synthesis (OMCOS)' has passed its golden age. Among the many transition metals used in organic synthesis, it is widely recognized at the present time that palladium is the most useful and versatile metal due to its ability to catalyze or promote useful reactions. Carbon-carbon bond forming processes are particularly interesting, as they are not always easy to achieve with other transition metal catalysts.³

I should say that the 1960s was the dawn of golden age of transition metal chemistry applied to organic synthesis. In my opinion, the chemistry of OMCOS has its origin in the following three industrial catalytic processes.

1. Carbonylation reactions, which include the $\text{Co}_2(\text{CO})_8$ -catalyzed hydroformylation of alkenes to give aldehydes, developed by Rölen in 1938, and two Reppe processes for producing acrylate from acetylene catalyzed by $\text{Ni}(\text{CO})_4$ and for the production of butanol from propylene catalyzed by $\text{Fe}(\text{CO})_5$ (1930–1940).
2. Production of polyethylene and polypropylene catalyzed by the Ziegler–Natta catalysts (the mid-1950s), and cyclization of butadiene catalyzed by either Ti or Ni catalysts to form COD (cyclooctadiene) and CDT (cyclododecatriene) selectively.
3. The Wacker process to produce acetaldehyde from ethylene catalyzed by PdCl_2 and CuCl_2 (1958).

I should emphasize that these processes, except polypropylene synthesis, had been invented and developed in Germany before and after the Second World War.

In 1962, at the Basic Research Laboratories of Toray, I was fortunate to have the opportunity to learn these commercial processes. Actually, I directly observed polymerization of ethylene and propylene using the Ziegler–Natta catalysts, as well as the Ni-catalyzed cyclization of butadiene to afford COD and CDT, being carried out by other groups in Toray. I was strongly impressed by the fact that the chemistry involved in these catalytic processes is completely different from the chemistry I learned earlier when I was working on natural product synthesis at Columbia. The new chemistry aroused in me a kind of culture-shock, I should confess. I realized clearly that the polymerizations of ethylene and propylene are extremely efficient carbon-carbon bond forming reactions. Also, macrocycles such as COD and CDT are obtained by the cyclization of butadiene without using high dilution methods. I had a firm conviction that the application of transition metal-catalyzed

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