

## Editorial

This special issue of SYNTHESES is dedicated to the memory of our friend, colleague, and mentor Jean Normant (1936–2016)



There is nothing more difficult and painful than to write the preface for a SYNTHESES issue that was originally planned to honor the 80<sup>th</sup> birthday of Jean Normant but had to be changed into a Memorial Issue. We, Jean's former co-workers, were initially supposed to give a few happy words for a special symposium at the University Pierre et Marie Curie, Paris VI, home university of Jean Normant, jointly organized by Dr. Christophe Meyer, Dr. Corinne Gosmini, and Dr. Frank Ferreira, on June 30<sup>th</sup> to honor Jean's 80<sup>th</sup> birthday.

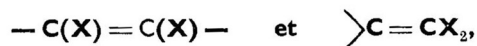
Unfortunately, our dear friend, colleague, and mentor Jean was taken away by cancer on June 9, 2016, three weeks before this event.

Born in Angers, France in 1936, Jean spent his early years there while his father Henri Normant was working on his PhD thesis under the supervision of Prof. Raymond Paul (Henri Normant had worked before for several years in Lyon with Victor Grignard). Jean then followed the family according to the appointments of Henri Normant. Jean started his studies at the high school 'Malherbe' in Caen before moving to Lille for a short period (1948–1951) and finally to Paris in 1953 where he graduated from high school. After a three-year period at the ENSCP (École Nationale Supérieure de Chimie de Paris), Jean decided to start a PhD thesis entitled 'Reactions of Grignard with organic halides, influence of polar aprotic solvents and particularly hexamethyl phosphotriamide' (HMPA, sometimes called the French solvent, was originally discovered by his father Henri Normant) under the supervision of Prof. Charles Prevost (1958–1963).

Several publications resulted from this period of research, the first one being 'Action of organometallic derivatives on dihalogenovinyl compounds' published in 1963 in the *Bulletin de la Société Chimique de France* (Normant, J. *Bull. Soc. Chim. Fr.* **1963**, 1868; see below for the first page of the paper).

N° 307. — Réactivité des organo-métalliques solvatés vis-à-vis des halogéno-éthyléniques et halogéno-acétyléniques (\*),

I. — Action de quelques organo-métalliques sur les composés dihalogénovinyles



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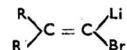
Les dichloro-1,2 alcènes :  $R-Cl=CHCl$  sont peu réactifs vis-à-vis des organo-magnésiens ; seul un solvant très « basique » (cas de l'hexaméthop) permet une réaction qui mène aux chloro-1 alcynes-1 :  $R-C\equiv CCl$ . Par contre, les dichloréthylènes *cis* et *trans* peuvent réagir dans le THF sur les organo-magnésiens à radical saturé, pour donner des chloro-1 alcènes-1 :  $R-CH=CHCl$  (mélange *cis*, *trans*). Les dichloro-1,1 alcènes :  $R-CH=CCl_2$  ne réagissent que s'ils sont activés par une fonction acétal ou étheroxyde située en  $\alpha$  de la double liaison.

I. — Généralités.

Hormis quelques structures particulièrement réactives, les dérivés halogénés se condensent mal sur les organo-métalliques. Les halogénoéthyléniques se montrent particulièrement inertes. Toutefois l'action des *organolithiens* dans ce domaine a fait l'objet de nombreux travaux et le comportement des halogènes « peu mobiles » a été bien précisé. Rappelons brièvement les principaux résultats de ces études :

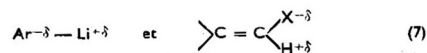
Dans un halogénoéthylénique, l'halogène a une mobilité bien moindre que dans un halogénure saturé en raison de la résonance de ses doublets libres avec les électrons  $\pi$  de la double liaison. La formation d'un anion  $X^\ominus$  devient ainsi difficile. Par contre, les hydrogènes fixés sur le carbone éthylénique sont nettement plus « acides » que dans le squelette saturé correspondant. Il en résulte une compétition entre l'échange lithium-halogène et lithium-hydrogène (3) soit, entre la métallation et la déshydrohalogénéation menant à un acétylénique. L'étude de l'action du butyl ou du phényl-lithium sur les dérivés du type :

montre la formation prédominante de l'acétylure de lithium dans les deux premiers cas, et de l'alcyne bisubstitué dans les deux suivants. Dans le dernier cas, on envisage la formation de :

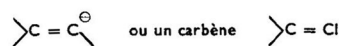


suivie de l'élimination de LiBr et migration du radical initialement en *trans* du brome, l'intermédiaire carbène étant contesté en raison de la stéricité de la réaction. Dans les autres cas le problème de l'élimination  $\alpha$  ou  $\beta$  a suscité un grand nombre de travaux dont il ressort que la *trans*  $\beta$  élimination est défavorisée par rapport à la *cis*  $\beta$  élimination (contrairement aux règles générales) cette dernière étant comparable à l'élimination  $\alpha$ .

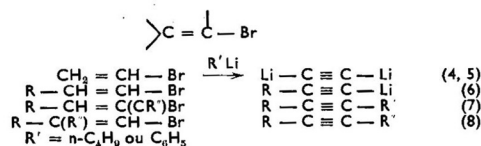
Toutefois, lorsqu'il existe un hydrogène sur le carbone porteur de l'halogène, il est possible de rendre compte des faits par un mécanisme concerté entre dipôles :



sans envisager un carbanion



Dans le cas contraire l'échange fonctionnel a lieu lentement : CURTIN (9) a par exemple préparé le lithien des bromostilbènes par action du butyl-lithium sur les bromostilbènes.



(\*) Thèse soutenue le 9 Mars 1963.

After his military service, spent at the Sorbonne (where Jean used his spare time writing and then editing his book 'Organic Chemistry Courses' published by Masson), he was appointed Assistant Professor in Reims (1964-1969) and in Paris (1969) where he rose to the rank of Full Professor in 1973 at the age of 37.

During one of our daily morning coffees, I asked him why he chose chemistry, a field in which his father had already excelled for a long time. To achieve recognition and make his first name would be even more difficult! To this rather naïve question, he told me how as a child he was fascinated by the expression in his father's eyes after a long and difficult day in his laboratory; some evenings they were full of happiness, at other times they were lost in deep thought. His father spent most of those evenings at his desk, endlessly scribbling molecules on reams of paper. Sharing in the excitement of the daily life of a leading figure in science awakened the interest and inquiring mind of a son.

From the beginning of his career, Jean was captivated by the synthesis and reactivities of organometallic compounds in organic chemistry, and he found, while preparing copper acetylide, that organocopper derivatives could add in a *syn* fashion across non-functionalized alkynes. The carbocupration reaction was born! This major contribution had worldwide applications, but it is interesting to emphasize that Jean made a major breakthrough in the research field of his father, the synthesis of vinylic organometallics, as he brought the stereoselectivity that was missing in the work of Henri Normant. After a long and intensive research period on the synthesis and reactivity of vinyl copper derivatives, the chemistry of copper carbenoids, including propargyl carbenoids, also started in his laboratory, and some very important fundamental applications were developed.

The development of the chemistry of organomanganese and organozinc derivatives as well as fluorinated organometallic chemistry was also initiated/developed in his research group. In the latter case, the control of the stereochemistry of the fluorinated double bond was a major achievement, particularly when considering the extreme importance of fluorine in therapeutic chemistry. Jean successfully introduced also the notion of chirality in his chemistry in the 1980s by combining organocopper reagents and chiral acetals. Among numerous examples of addition reactions of an organometallic species to an olefin, the addition of an allylic zinc reagent to a vinyl organometallic is particularly striking and uniquely, useful synthetically. I remember with delight all these hours spent with Jean on the blackboard and in a cloud of smoke, trying to understand and predict these often capricious, but always selective and clean, reactions. Later, we concentrated on the carbometallation reaction of unactivated olefins, first intramolecularly through organozinc derivatives, then intermolecularly where we brought a vital element to modern chemistry by introducing asymmetric catalysis when adding organolithiums to isolated double bonds.

All over his life, Jean was doing experiments himself in his small laboratory on the back-side of his office, and it was frequent that we were discussing science with him in his lab while he was purifying a freshly prepared compound by distillation with a Bunsen burner. We all learned the art of distillation with a flame!

During all these years, Jean attracted an increasing number of students from France and abroad to his laboratory. He supervised a very large number of PhD theses and most of those students now hold academic positions. In his 41 years of scientific activities, he published more than 360 scientific articles in international journals and gave around 200 lectures worldwide, particularly in Japan, where he built numerous professional and personal relationships.

Jean's pioneering contributions have earned him an outstanding international reputation and have helped put French science in the spotlight. As a result, Jean has received numerous national and international awards, including the French Chemical Society Adrien Award (1963), the Foundation Van't Hoff Award (1967), the French Society of Chemistry Lebel Award (1990), two prizes of the Academy of Sciences (1979 and 1987), and the silver medal of the CNRS (1979). He was also elected as a member of the Academy of Sciences (1993) and was a Centenary Lecturer of the Royal Society of Chemistry (2000). He has obviously served on several national committees, although he never enjoyed administrative duties, and was a board member of many journals.

One of Jean's characteristics was his daily reading of scientific literature, always in a cloud of smoke, far beyond the boundaries of his immediate research. Without requesting, Jean taught us the importance of reading literature on a daily basis by using what we called 'Jean's tactic': During our daily morning coffee, Jean used to share his scientific thoughts and feelings about recent literature and asked for our opinion on the last published papers he read. To be able to share his excitement and participate to the discussion, it was better for us to read the papers before him!

I will always remember Jean reading these tiny lines of chemical formulas in Chemical Abstracts – in case he could find something new (and he did many times!). As a fresh PhD student, I thought that if I want to be a good scientist, I had to do the same and started to also read Chemical Abstracts. But I have to confess that I couldn't hold this treatment too long and stopped after a month... and kept myself busy with all the other 'more human' journals.

In 1993, when Jean was elected a member of the French Academy of Sciences, I had the pleasure of being invited to the ceremony. I will always cherish the memory of Henri and Jean, father and son, both academicians, standing next to each other under this beautiful cupola. This is an extremely rare case in the French scientific history.

One could not conclude this preface without talking about the man himself and his strong human qualities. Besides being extremely fair, honest, and humble, Jean was a warm and particularly attentive person. He always listened and patiently advised his students, showing considerable respect and tolerance, even when they made mistakes.

Over the years, countless friends, colleagues, and visitors have enjoyed the hospitality of the Normant household. Most of us have fond memories of excellent meals, outstanding wines, and liberal doses of anecdotes. Every one of us who has worked with him knows how important his family was to him and how supportive his wonderful wife, Catherine, has been throughout all his life. Unfortunately, his 'Chère Catherine' as he used to say, disappeared too early and left Jean alone for the last decade with his three children Emmanuel, Alain, and Claire.

Undoubtedly, his devotion to research and teaching has influenced and will continue to influence everyone fortunate enough to know him. Many of us try to adhere to the 'Jean Normant' style in our academic endeavors.

I may summarize his style by only two quotes for the youngest generation:

- 'Do not be afraid of the international competition, it is a clear sign that what you are doing is important.'
- 'Do the best possible science you can, recognition will come out of it. It may take longer than using different paths, but it will always be long-lasting...'

On behalf of all his former co-workers, his many friends and colleagues, of the French chemical society and of all the authors of this special issue of SYNTHESIS, we would like to express our deepest recognition and admiration to Jean. And while I will miss him as a mentor and as a close friend, I am comforted by the fact that his accomplishments, his role model, the Jean's school of organometallic chemistry will continue to exemplify the very best in Science.

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