Book Review

The Barbier Reaction and Related One-Step Processes. By Cornelis Blomberg. Springer-Verlag: Berlin, 1993, 183 pp., hardback DM 186. ISBN 3-540-57169-8.

This monograph offers a pleasurable review of the one-pot reactions of organic halides and mainly carbonyl compounds carried out especially in the presence of stoichiometric amounts of magnesium. Such a process is usually called the Barbier reaction but in agreement with the author, is it the judicious name?

The book carries the reader away on an exciting trail concerning an in depth historical approach to this reaction and related ones. The initial discovery by E. Frankland of alkylzinc in 1849 was followed by synthetic applications by well-known chemists such as Beilstein, Saytzeff, Reformatsky, while W. Hallwachs and H. Schafarik prepared dialkylmagnesium compounds as early as 1859. The one-step preparation of a tertiary alcohol from a ketone and iodomethane using magnesium instead of zinc was reported by Philippe Barbier at the end of the nineteenth century (1899). One year later, his student, V. Grignard opened the twentieth century with the introduction of the two-step procedure which has led to the now widely known "Grignard reagents" or more reasonably, to the "Barbier-Grignard reactions".

As pointed out by the author, the euphoria to the reagent of the Nobel-prize winner has in part blinded chemists to the Barbier reaction for some time. Therefore, more work has been published where the two-step procedure was used rather than the more comfortable one-step one. Nevertheless, the one-step methodology has constantly attracted synthetic chemists particularly those from industry. Therefore, the story continues all through the book with the introduction of different metals: sodium, lithium, zinc, tin, aluminium, lead, bismuth....,

occasionally in the presence of activating agents such as palladium or nickel catalysts, and various choices of solvent (even aqueous media under sonication). Thus, it becomes possible to react almost any organic halide with aldehydes, ketones, esters, carbonates, epoxides, nitriles, phosphonates, acetals.... or to carry out intramolecular Barbier-type reactions. Furthermore, some procedures can be used for the synthesis of organometallic compounds (Si, Ge, B). But the story is not finished with the end of the monograph. Indeed, one of the last chapters concerns the mechanism: a definitive answer cannot be presently proposed despite the large review of work dedicated to this topic.

Comparisons between the results and the mechanisms of the Barbier-type reactions and the two-step ones are often proposed. A profusion of illustrations and clear compiling tables are provided, allowing a relatively easy choice between the different possibilities before carrying out a "Frankland-Saytzeff-Barbier-Grignard reaction". Furthermore, a worthwhile chapter concerns the experimental conditions and various procedures to activate magnesium, lithium and zinc. I regret that there is no subject index but the table of contents is well organized.

Throughout the pages, the author has tried to draw our attention to the advantages of the Barbier reaction and related processes. In my opinion, he has well succeeded thanks to a clear, impressive and almost up-to-date presentation providing an overview of the one-step processes. Thus, I recommend this excellent book, easy to read to anyone interested in organic and organometallic chemistry.

Jacques Muzart, CNRS/University of Reims Champagne-Ardenne, France.

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