Reaction Mechanisms of Organometallic Compounds; by O. A. REUTOV AND I. P. BELETSKAYA, North-Holland Publishing Company, Amsterdam, 1968, xi+466 pages Dfl. 85.– (Distributed in the Western Hemisphere by Wiley & Sons, New York).

A monograph on a subject by one who has largely created it has charm for that reason. The reviewer's favourite book on the Walden inversion is Walden's, even though, written in1913, the subject had no theory. Much more important than that is the fact that the book was not merely written but lived by Walden, as one can feel in every page. The first monograph on a major new field should be written by its prime creators, because nothing can dim the freshness of first-hand treatment. The opportunity to offer such treatment is not always taken by the right people at the right time, but in Reutov and Beletskaya's book, the first comprehensive monograph on reaction mechanism in organometal chemistry, the ideal conditions for first exposure of a new field are fulfilled. These investigators' initial interest and first ideas were derived from Nesmeyanov's school of chemistry, but it was they and their immediate colleagues who developed from this starting point a school of reaction mechanism in the organometal field, and who brought into routine employment the physical methods on which such a subject must experimentally depend.

For anyone who wants to read what is now known of the reactions of organometal chemistry beyond their mere stoicheiometry, this is the book he requires. Its length is nicely judged. The treatment is full, but quite digestible. And it is authoritative.

Most of the reactions treated are either electrophilic or homolytic substitutions (or additions leading to substitution), the former predominating. A carbon–metal bond fission, if heterolytic and unaccompanied by other covalency changes, would lead to a carbanion; but because of the polarities developed other bond changes often become synchronously involved with the result that carbanion formation is by no means a universal first step in heterolytic organometal substitutions. Homolytic carbon–metal bond fission is in a different case. It is less liable to become elaborated into a bimolecular or higher system of bond changes, and so a free carbon radical really is formed in this case as an intermediate of principle in a first (or very early) step in homolytic organometal substitutions. Reutov and Beletskaya's book opens with a survey of the concept of carbanions, although, as in made clear later, the position of carbanions in electrophilic metal displacement is much more theoretical and partial than is that of carbon radicals in homolytic reactions. The intermediacy of carbanions has been kinetically demonstrated (first by the authors of the book) in a few tailor-made examples in which Nature has been constitutionally encouraged to fall back on a carbanion intermediate, whilst in many more examples it has been equally firmly proved that carbanion intermediates are not produced. One may feel that it would have been in order to include at this point some short survey of carbon radicals, inasmuch as they really are inescapable intermediates in homolytic organometal substitutions.

The main part of the book begins with the second chapter. This chapter is not only the longest, but may be considered as the most important, because it deals with metal-for-metal substitutions in alkyl metals, potentially one of the greatest fields of reactions of simple molecules and ions because it embraces the replacement of any of the eighty metals by any other in combination with carbon in any type of organic system. One of the most obvious characteristics of the treatment, both in this chapter and the subsequent ones, is its thoroughness and good order, which make the relationships between the different families and sub-families of reactions very easy to follow. Studies of the kind treated in this book are usually summed up in an attempt to describe some features of a mechanism that could account for the observations; but ambiguities of interpretation are often possible. The authors have dealt with this situation in a very impartial way, outlining the picture which the observations suggested to the original observers, and mentioning any alternative interpretations offered by others, and then the authors' own interpretation if significantly different. The whole account, though legitimately historical, is a little longer than it need have been. For instance, it need not have included citations of explicitly withdrawn or much altered conclusions, particularly without reference to the circumstance that their status had been completely changed. Another minor comment on the treatment is that it might have been helpful to separate electrophilic substitution at saturated carbon from substitution at unsaturated, including aromatic, carbon. The mechanisms are expected to differ substantially. It will not be an accident that the only known examples of "four-alkyl" mercury exchange employ aromatic groups.

The rest of the book, excepting the last chapter, deals on similar lines with other great families of reactions in which particular types of electrophilic substituting agents, such as halogens, or acids, effect substitution, causing the displacement from carbon of metal, or in some cases, non-metal substituents. The treatment has the same clarity and good order, and the same informative but easy reading, which characterises the already discussed treatment of metal exchanges. The chapter on halide–metallation contains excellent accounts of the work of Eaborn on these reactions in application to organic compounds of the Group IV elements, of Kuivila with respect to organoboron compounds, and of Reutov and Beletskaya and their colleagues in reference to organomercury compounds. In the treatment of all this work, a clear distinction is kept between substitution at a saturated and at an unsaturated carbon atom. A point of special interest is that homolytic processes can play a notable part in demercuration by iodine and bromine. Protodemetallation, that is, the acidolysis of metals, is the subject of another long chapter. It provides another rich field, comparable to halodemetallation in its variety and interest.

Not much need be said about the last chapter, because it is not a normal continuation of the theme of the book, but is essentially an appendix of reference material. It comprises a record of physical properties, mainly polarographic, spectral and dipole moment properties, of inorganic and organic mercury(II) compounds. The tables of data are quite extensive. For the investigator in the field, they are bound to be most useful. For the general reader, the important thing is to know that they exist and where to find them.

C. K. INGOLD