

**Houben-Weyl Vol. E10 Organo-Fluorine Compounds. Methods of Organic Chemistry.** Edited by B. Baasner, H. Hagemann, J. C. Tatlow. Thieme: Stuttgart, 2000, 5 volume set. E10a: 740 pp, ISBN 3-13-116664-9; E10b/1: 720 pp, ISBN 3-13-119064-7; E10b/2: 896 pp, ISBN 3-13-119164-3; E10c/1: 800 pp, ISBN 3-13-1264044-0; E10c/2: 800 pp, ISBN 3-13-126324-5. Hardback DM 3,300 per volume. Softback DM 378 per volume.

These comprehensive volumes fill a gap in the chemical reference literature on the increasingly important topic of organo-fluorine chemistry. The up-to-date collection of methods and reagents in the three first volumes (10a, 10b/1 and 10b/2) would be excellent material for back-to-back reading, if one was ever fortunate enough to have the time. Used as a reference text or for occasional browsing, it is equally useful and informative. The volumes are didactically well-constructed and overall very readable. Both the one-time user and the specialist can find details and references on the preparation, analysis, reactivity and safety of fluorinated products.

The introduction gives a broad and in-depth overview over the history of fluorine chemistry, nomenclature, properties, analysis, structure determination and applications of organo-fluorine compounds. It could have been worthwhile to include tables with key NMR-data in the given overview on  $^{19}\text{F}$ -NMR-analysis to avoid the reader having to use a second reference source.

The main body of volume E10a is primarily concerned with the formation of carbon-fluorine bonds. A detailed description is given of all types of fluorinating agents from inorganic salts or complexes to organic reagents, accompanied by tables on applications, apparatus and reaction conditions. However, the reagents and their features are not all treated with the same elaborateness. For example, the uses of  $\text{SF}_4$  are described extensively whereas  $\text{F}_2$  is mentioned rather sparsely, in spite of the increasing occurrence of selective fluorinations using  $\text{F}_2$  in the literature as well as its growing industrial importance in specialized companies.

Necessarily in a compilation this size, some sections appear slightly rushed, such as 6.4.9 on *New Fluorinating Agents*. No systematic distinction is made between the substantially different electrophilic and nucleophilic reagents, and none of the newer nucleophilic reagents are mentioned at this point. A gap is evident where complex fluorides such as  $\text{HF}_2^-$ ,  $\text{H}_2\text{F}_3^-$  etc. appear in parts in the chapters on *Hydrogen Fluoride* and on *Alkali Fluorides* rather than being discussed systematically. We didn't quite understand why the area of organo-fluorine chemistry in general was introduced again in chapter 14 on *Alkali*

*Fluorides and Special Methods*. Overall, however, given a little time for browsing, this volume is well-organized and can be very inspiring to the investigative mind.

Volumes E10b/1 and E10b/2 give an extensive overview over the academic and patent literature of the 1990s dealing with the synthesis of organo-fluorine compounds. The focus of these volumes lies on a classification of reaction types and is accompanied by numerous examples and preparative detail.

Volume E10b/1 starts with synthetic methods using fluorinating agents that keep the carbon skeleton unchanged (substitution and addition reactions applicable to both aliphatic and aromatic compounds). We found some overlap with volume E10a, particularly with regard to  $\text{SF}_4$ -chemistry, fluoro-dediazoniation and addition of fluoride to  $\text{C}=\text{C}$ -bonds.

Chapter 2 deals with the synthesis of fluorinated compounds starting from other organo-fluorine compounds ("building-block approaches"). The methods are listed according to whether the carbon skeleton is preserved or not, and are sorted depending on the type of C-C-bond formation. These include substitution reactions based on fluorinated synthons which contain a group-IV element (e.g.  $\text{CF}_3\text{SiMe}_3$ ) or a group-V element; condensation reactions (e.g. with carbonyl compounds like  $\text{CF}_3\text{CHO}$ ); organo-metal-strategies, which utilize a number of perfluorinated reagents; radical addition reactions onto alkenes and alkynes; cycloaddition reactions; dimerization reactions; syntheses of systems containing carbon-heteroatom bonds (C-S, C-P, C-N); and the degradation of fluorinated precursors by skeletal bond-cleavage reactions.

Volume E10b/2 continues along the same lines by describing oxidation reactions, intramolecular dehydro-halogenation and dehalogenation, isomerization and disproportionation, all specific to organo-fluorine compounds. Furthermore, the volume contains a review on the reactivity and stability of organo-fluorine compounds. The steric and electronic effects of fluorine in carbanions, carbocations, carbon-centered radicals and carbenes are described. Subsequently, the different possibilities to cleave C-F bonds are treated: replacement of F by H, loss of F to form  $\text{C}=\text{C}$  bonds; replacement of F to form C-O bonds; elimination of F to form C-S bonds; elimination of F to form C-N bonds. At the end of volume E10b there are very useful and detailed indexes on authors, formulae and references to over 350 reviews and monographs, organized by topics.

Volumes E10c/1 and E10c/2 are meant as a comprehensive index of the Houben-Weyl E10 series about organo-fluorine compounds.

The index consists of a tabular compilation of all methods for the preparation of organo-fluorine compounds collected in the Houben-Weyl volumes. The methods are classified by the type of bond-forming or bond-breaking reaction in a clear and easy-to-find format. However, an arrangement according to product classes might have been more useful when looking up a preparative method

for a particular structural element. There seems to be no good way of searching for a reaction from a specified substrate A to the corresponding product B. We tested the index by looking for an answer to the question “How can  $\text{OCF}_3$ -groups be synthesized?” and failed. The table of contents at the beginning of E10b was more helpful. Oddly enough, none of the abundantly used abbreviations are listed here, in contrast to E10a and E10b, where even the most straightforward abbreviations like HF are explained.

To conclude, the Houben-Weyl volumes on organo-fluorine compounds give a broad overview over both traditional and modern methods; however, this survey is not totally exhaustive. Some chapters are more up-to-date than others, covering the literature from the beginnings of

fluorine chemistry up to between 1992 and 1998. The volumes are not entirely devoid of mistakes, but these are usually obvious and do not reduce the great value of Houben-Weyl E10 to all synthetic chemists, whether specialized in fluorine chemistry or not. The compendium is exceedingly readable, concisely structured and well-illustrated.

We are certain that this piece will occupy a central position on the library shelves of most academic and industrial groups active in synthetic organic chemistry.

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