

Professor Józef Drabowicz

A Tribute



This special issue of Arkivoc is dedicated to Professor Józef Drabowicz on the occasion of his 76th birthday, to acknowledge his contribution to hetero-organic chemistry and his activity for the hetero-organic chemists' community

Professor Józef Drabowicz belongs to a limited group of Polish chemists who are well recognized internationally. His work has been carried out over 50 years in cooperation with Professor Marian Mikołajczyk and has made a noticeable contribution to the development of heterorganic chemistry. His name became internationally recognized as a result of many pioneering works on the stereochemistry of hetero-organic derivatives, in particular compounds with a stereogenic sulfur atom. The recognition is justified thanks to the following factors.

- a) Frequent invitations by editors of well-known book series to prepare monographic chapters. In total, he co-authored 46 chapters published, in *The Chemistry of Functional Groups* (Patai and Rappaport), *Houben-Weyl, Science of Synthesis*, *Comprehensive Organic Functional Group Transformations II*, *Comprehensive Heterocyclic Chemistry* and *Advanced Heterocyclic Chemistry*.
- b) Entrusting him as editor of two volumes (33 and 39) of the prestigious publishing series "Science of Synthesis-Update" and membership on the Editorial Boards of "The Open Inorganic Chemistry Journal" (2007-2011) and "ISRN Organic Chemistry" (from 2010 r.), *Phosphorus, Sulfur and Silicon and the Related Elements* (from 2015), *Current Green Chemistry* (from 2018), *Current Organic Chemistry* (2020), *Molecules* (2020) and *Materials* (2021)
- c) Invitations to deliver lectures at international and national scientific conferences (more than 40 invitations in total),
- d) A large number of invited lectures to foreign universities and industrial laboratories (over 100 invited lectures - Japan, Germany, Italy, France, Denmark, Hungary, Belgium, Spain, USA)
- e) Invitations as "visiting professor" by the universities of Bologna, Halle and Caen plus invitations to carry out short-term study visits by foreign research institutions (universities of Hiroshima, Tokyo, Kyoto, Wakayama, Tsukuba, Sheffield, Milan, Budapest, Halle, Bochum, Greiswald, Berlin, Odense, Caen, Gent, Reims, Florence, Cagliari and Bilbao; also by the National Research Centre in Cairo and the UAN Institute of Organic Chemistry in Kiev).

Prof. Drabowicz was born in 1946 in Działoszyn (Poland) and studied at the University of Lodz (M.Sc. in 1969). Since then he has been employed at the Centre of Molecular and Macromolecular Studies (CMMS), Polish Academy of Sciences in Lodz. He was awarded his PhD under the supervision of Professor M. Mikołajczyk in 1975 and D. Sc. (habilitation) (Lodz University, 1987). Since 1998 he has been Professor at the Centre of Molecular and Macromolecular Studies. Since 2002 he has taught simultaneously at the Jan Długosz University in Częstochowa, where during 2008 -2016 he served as Vice-Rector for Science and Research. He spent his postdoctoral stay at the University of Tsukuba, [with S. Oae (1976-1977)] and worked for 18 months as a Research Associate with Professor J. C. Martin at Vanderbilt University, Nashville (1989-1990).

Overview of research achievements

The scientific interests of Professor Drabowicz include chemistry and stereochemistry of hetero-organic compounds, synthetic methodology, asymmetric synthesis and material chemistry.

In January 1975 Józef Drabowicz defended his doctoral thesis entitled "Stereochemistry of some sulfinyl derivatives". The research described in the dissertation concerned pioneering attempts of non-classical optical separation of compounds with stereogenic heteroatom sulfoxides^{1,2}, sulfinate esters³, thiosulfinates² (Figure 1), and phosphine oxides by creating inclusion complexes with β -cyclodextrin.

Optical resolution via inclusion complex (1978)

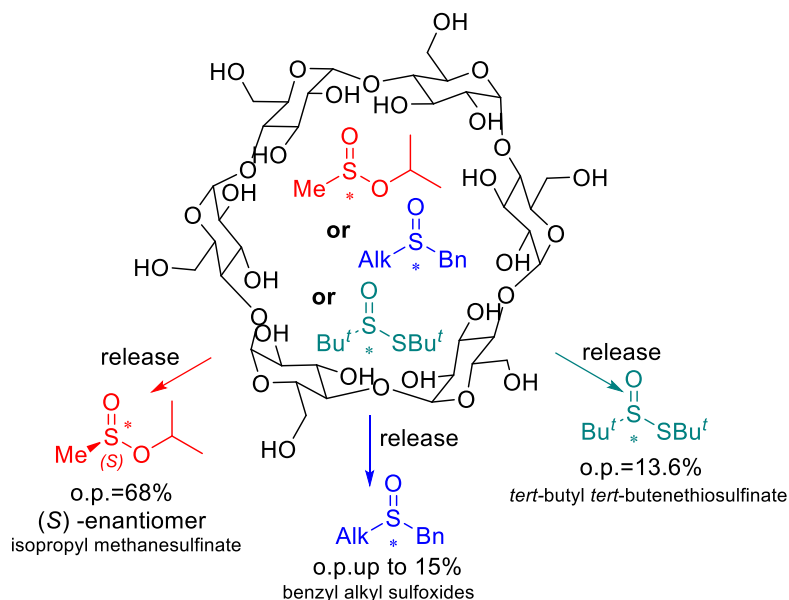
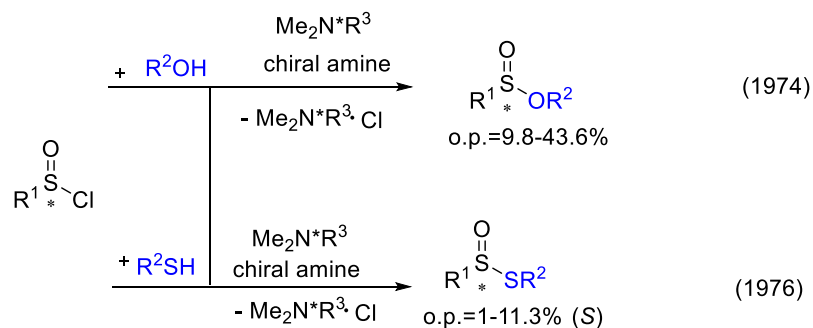


Figure 1. Non-classical optical resolutions of chiral sulfinyl compounds via β -cyclodextrin inclusion complex.

Pioneering aspects included a general method for the asymmetric synthesis of *O*-alkyl alkane(arene)sulfinates⁴ and thiosulfinates⁵ (Figure 2).

$\text{Me}_2\text{NR}^3 = (+)$ - or $(-)$ -*N,N*-dimethyl- α -phenylethylamine, $(-)$ -*N,N*-dimethylmenthylamine, or $(+)$ -*N,N*-dimethyldehydroabietylamine



$\text{Me}_2\text{N}^*\text{R}^3 = (-)$ - *N,N*-dimethylamphetamine; $(+)$ - *N,N*-dimethyl- α -fenchylamine;

Figure 2. Asymmetric condensation of sulfinyl chlorides with achiral alcohols/thiols in the presence of optically active tertiary amines leading to optically active (thio)sulfinate esters.

It is worth noting that the reaction of sulfinyl chlorides with alcohols or thiols (which in principle could be extended to other heteroatoms) is the first enantio-differentiating transformation described in the chemical literature, now referred to as "DKR reactions" (dynamic kinetic resolution). The research described in the doctoral dissertation also led to new groups of optically active sulfurous acid [sulfuric (IV)] acid derivatives, namely amidosulfites, amidothiosulfites⁶ (Figure 3(1)), and aminosulfinyl chlorides⁶ (Figure 3(2)), which are still the only group of optically active sulfinyl halides described in the literature.

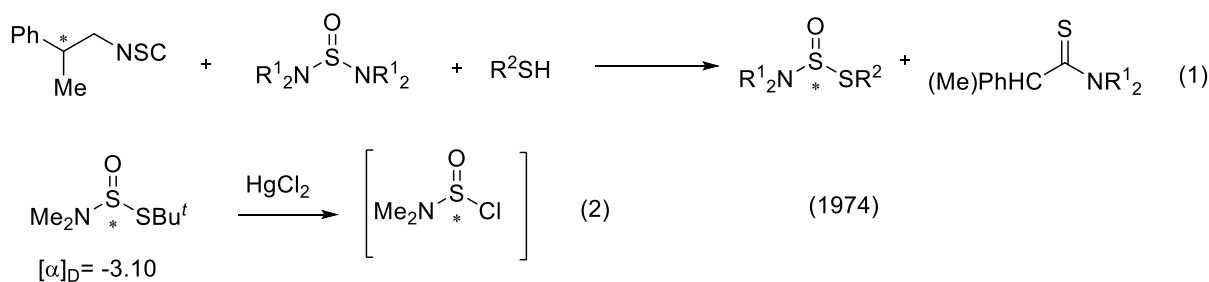


Figure 3. Asymmetric synthesis of amidothiosulfites. Reaction of (-)-*t*-butyl dimethylamidothiosulfite with mercury(II) chloride leading to optically active dimethylaminosulphinyl chloride with retention of configuration at the sulfinyl centre.

In the years 1976-1977, Dr Drabowicz during a one-year postdoctoral fellowship in the team of Prof. S. Oae, conducted a series of studies on the synthetic and physicochemical aspects of the transformation of selected organosulfur derivatives.⁷⁻⁹

The research, constituting the basis of his habilitation thesis led, *inter alia*, to the development of a useful modification of the classical method of synthesizing optically active sulfoxides with high enantiomeric excess and new asymmetric and stereoselective procedures for the syntheses of optically active sulfinyl esters and thiosulfonates. Another achievement of Prof. Drabowicz, of fundamental importance for the dynamic stereochemistry of sulfur, was the discovery of a unique stereochemical course of acid-catalyzed alcoholysis of optically active sulfinamides¹⁰ (Figure 4).

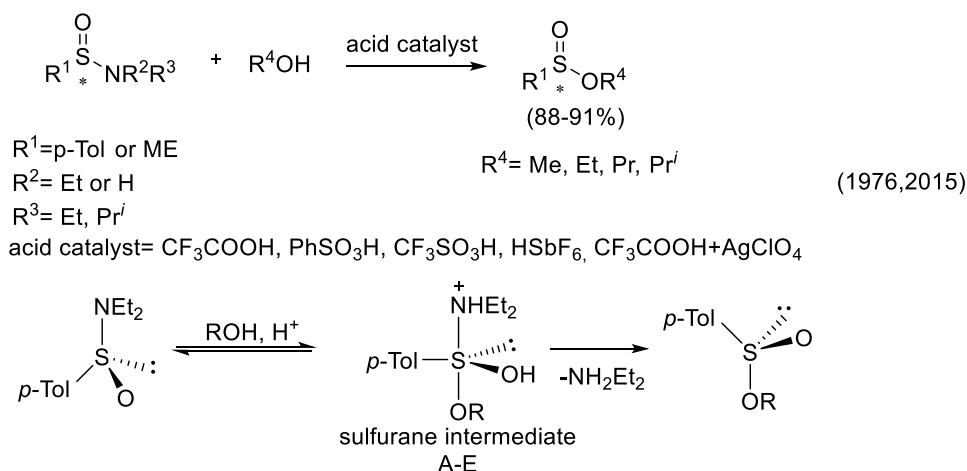


Figure 4. New synthesis of optically active sulfinates.

The study of the mechanism of this and other reactions of compounds with a stereogenic sulfur atom allowed the formulation of a general mechanism of nucleophilic substitution in organosulfur compounds and the establishment of the addition-elimination mechanism with the participation of sulfuranes as intermediates.¹¹ In the years 1989-1990, he worked for 18 months as a "research associate" in the group of Prof. J.C. Martin at Vanderbilt University in Nashville. At that time, he carried out his own research project aimed at developing methods of synthesizing optically active hypervalent organosulfur compounds (Figure 5) to explain the mechanisms of their thermal and organic acid-catalyzed racemization.^{12,13} Since 1990, he has

continued research related to the chemistry and stereochemistry of organosulfur compounds, in particular hypervalent derivatives (Figure 6).

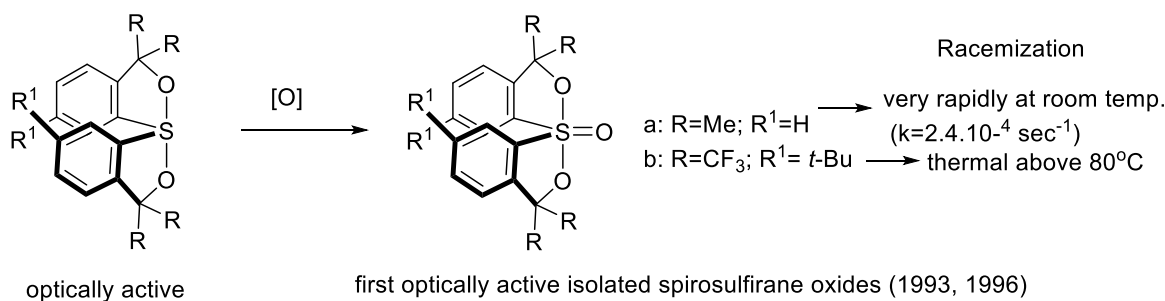


Figure 5. Stereoselective oxidations of the parent chiral sulfurananes.

He succeeded in preparing the first enantiomerically pure, C_2 -symmetric spiro-selenurane¹⁴ (Figure 6, left) and developed an approach to isolate optically active oxide analogues of the selenurane (Figure 6, right) via enantioselective liquid chromatography of racemates or by optical resolution occurring during the slow evaporation of acetonitrile solutions.¹⁵

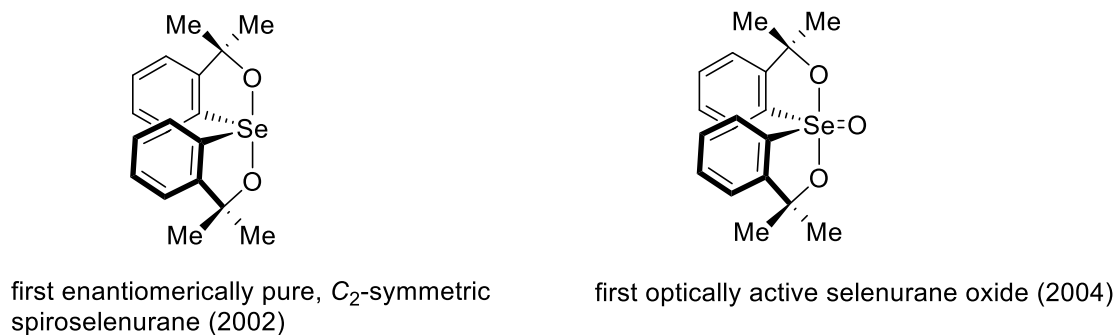


Figure 6. The first enantiomerically pure, C_2 -symmetric spiro-selenurane and the first enantiomerically enriched selenurane oxide.

He carried out parallel methodological research in the field of organic and asymmetric synthesis supplemented by works on the synthesis of compounds of "new materials" and the use of selected spectroscopic techniques (NMR, CD, VCD) in structural studies. Recently, Prof. Drabowicz began research on the use of flow techniques in the chemistry of hetero-organic compounds^{16,17} and chiral polythiophene systems functionalized with substituents with stereogenic heteroatoms (Figure 7) as substrates in the synthesis of conductive organic materials.^{18,19}

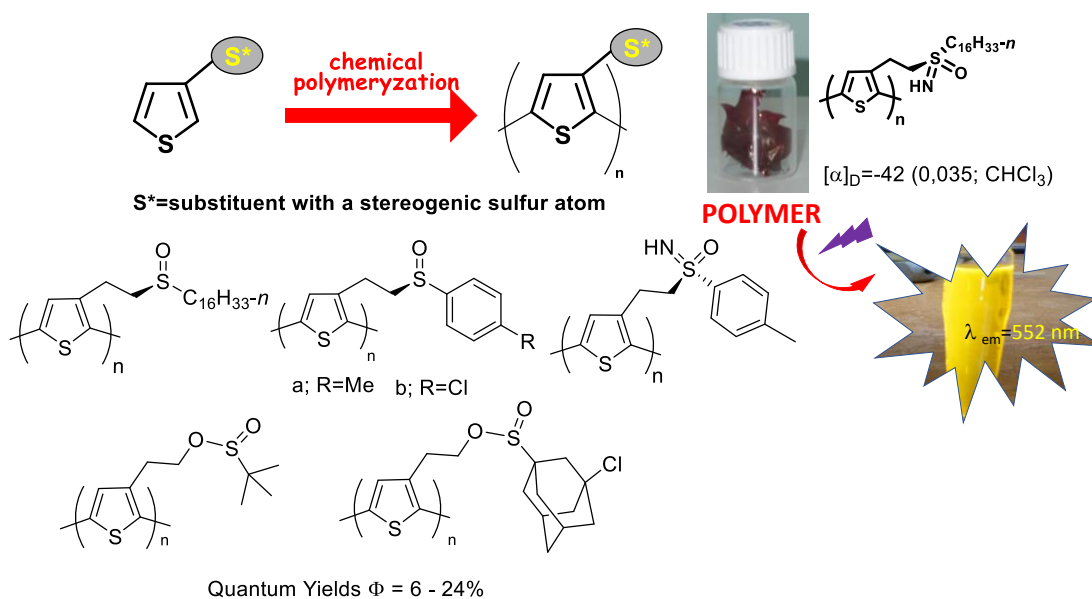


Figure 7. Chiral polythiophenes functionalized in the 3-position of the thiophene ring with a pendant containing a stereogenic sulfur atom of sulfoxides, sulfoximines or sulfinates.

After 1990 he was a coordinator of several national grants, including a «Maestro» grant of the National Science Center and was also a partner in 2 EU grants. For many years, fragments of these studies have been carried out in cooperation with domestic and foreign groups (including the teams of Professors Stevens, Yamamoto, Polavarapu, Santi and Soloshonok). The research achievements of Prof. Drabowicz have been described so far in over 170 original publications. A number of them in prestigious chemical journals such as *J. Am. Chem. Soc.*, *J. Org. Chem.*, *Chem. Commun.*, *Tetrahedron*, *Tetrahedron; Asymmetry*, *Synthesis*, *Synlett*, *Chem. - A European Journal*, *Green Chemistry*). This publication output is complemented by the co-authorship of over 40 review articles and over 40 monographic chapters. Prof. Drabowicz is also co-author of one book [*Chiral Sulfur Reagents: Applications in Asymmetric and Stereoselective Synthesis*, CRC Press, Boca Raton, USA, 1998 together with M. Mikołajczyk and P. Kiełbasiński] and 18 patents. The international recognition of scientific research conducted by Prof. Drabowicz is clearly evidenced by the fact that his co-authorship and authorship are often cited in the chemical literature and monographic publications. According to the Web of Knowledge data (as of April 27, 2022), the total number of citations (excluding self-citations) is over 3,100 with an index of $H = 33$. Very recently his name appears on the list of 2 percent of the most influential scientists in the world in terms of citation of their publications prepared by Stanford University in cooperation with Elsevier. The significant scientific achievements of Professor Drabowicz are crowned by many awards, for example the Award of the Minister of Science and Higher Education for lifetime achievement in scientific research, granted in 2015; the Kostanecki Medal of the Polish Chemical Society, awarded in 2011 at the 54 Meeting of the Polish Chemical Society in Lublin; the Award of the Scientific Secretary of the III Division of the Polish Academy of Sciences- granted in 1981; Awards of the Scientific Secretary of the Polish Academy of Sciences received in 1970, 1972, 1974, 1976 and in 1988; The Polish Chemical Society Award for Young Chemists -received at the 18th Meeting of the Polish Chemical Society -in Opole, 1975.

Overview of activities aimed at heteroorganic chemistry community

Prof. Drabowicz is a member of the International Advisory Boards of the International Conference on the Organic Chemistry of Sulfur (since 2012), the International Symposium on Halogen Chemistry [(HALCHEM) since 2012) and the International Conference on Phosphorus Chemistry (since 2018). He was Chairman of the 25th International Conference on the Organic Chemistry of Sulfur (ISOCS-25) and HALCHEM VII held in Czestochowa (Poland) in 2012. and 2015 He co-chaired the 23rd International Conference on Phosphorus Chemistry held on line in Czestochowa in 2021. This year he plans to organize in Lodz the 9th Workshop of the multidisciplinary network SeS Redox and Catalysis. In the years 2002-2019, Prof Drabowicz was the main organizer of annual international conferences devoted to heterorganic chemistry: International Symposium "Advances in the Chemistry of Heteroorganic Compounds" and „International Symposium on Selected Problems of Chemistry of Acyclic and Cyclic Heteroorganic Compounds. This year, after a 2-year hiatus caused by the COVID 19 epidemic, these two conferences will be organized again. Prof. Drabowicz has supervised more than 25 research students (PhD, Master and undergraduate students). He has been involved also in grant reviews in Hungary, Romania and Latvia.

Personally, but also as scientists professionally associated with Professor Drabowicz, we are pleased to say that he is cordial towards his co-workers and colleagues and that he offers a helping hand to everyone. We have always admired his commitment and devotion to scientific work. It should be added that he always points out that his scientific activity could not have been realized without the understanding of his wife Anna (they recently celebrated their 49th year of marriage), two daughters Ola and Kinga and son Tomasz. Since 2003. He has been the happy grandfather of Jan,-19 and Konrad 16. He only complains that the long distance between Łódź and Essen (Germany), where they live, limits the possibility of more frequent meetings with them and his daughter's family.

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Selected publications

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<https://www.scopus.com/authid/detail.uri?authorId=7003887042> or <https://orcid.org/0000-0002-4899-5970>).

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