

## Professor Anastasios Varvoglis

### A Tribute

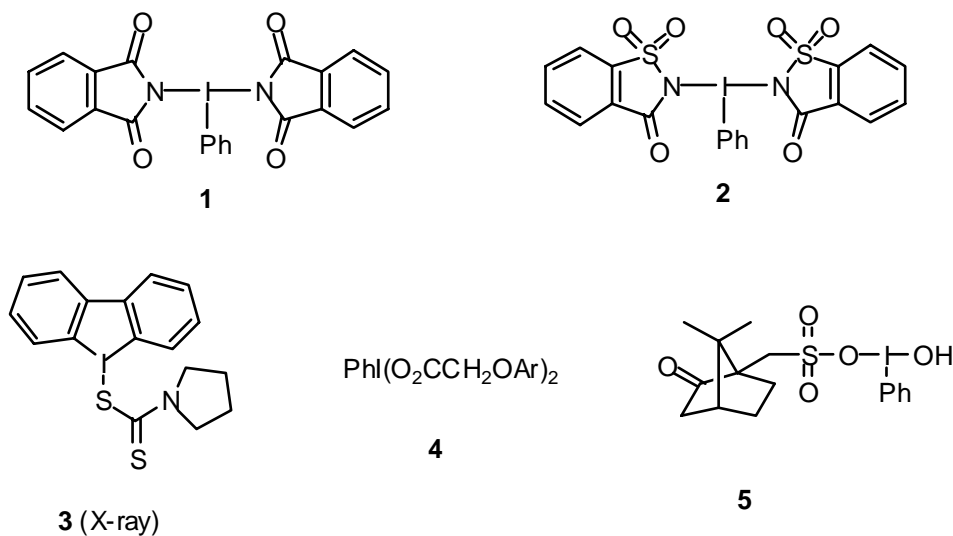


Anastasios Varvoglis (Tassos) was born in Athens, Greece, on the last day of 1938 (December 31, 1938). He studied chemistry at the University of Thessaloniki (1956-1961). A part of his long military service (30 months) was spent at the Nuclear Research Center "Democritus", in Athens, where he had his first three publications in radiochemistry, concerning with the behavior of organic bromides upon neutron-irradiation.<sup>1-3</sup> After winning a national scholarship, Tassos went to Cambridge University to study for his Ph.D. (1964-1967). He worked there under the supervision of the then young lecturer A. J. Kirby on the synthesis and hydrolysis of phosphate monoesters derived from acidic phenols. This research resulted in several important publications,<sup>4-9</sup> including a fundamental, full paper<sup>5</sup> in *J. Am. Chem. Soc.* on the reactivity of phosphate esters and a review<sup>9</sup> on the organic chemistry of phosphorus. Returning to Greece, Tassos obtained the position of lecturer in organic chemistry at the University of Thessaloniki. He became a full professor in 1976; when he retires, in 2006, he will have completed 39 years of service at this University, apart from his undergraduate studies. The main area of his research in Thessaloniki is the development of hypervalent iodine chemistry. Professor Varvoglis was the supervisor of eight predoctoral fellows, three of which are presently professors in Greece and one in USA. Also, many of his undergraduate students have become professors in Greece, USA and France.

Professor Varvoglis has played a key role in the unprecedented resurgence of hypervalent iodine chemistry during the last two decades of the 20th century. Since his first publication,<sup>10</sup> in 1972, dealing with an unusual reaction between triethyl phosphite and diphenyl iodonium iodide, he continued almost exclusively to work in this field. The following sections provide a brief description of the most noteworthy areas of his research activities over the last three decades.

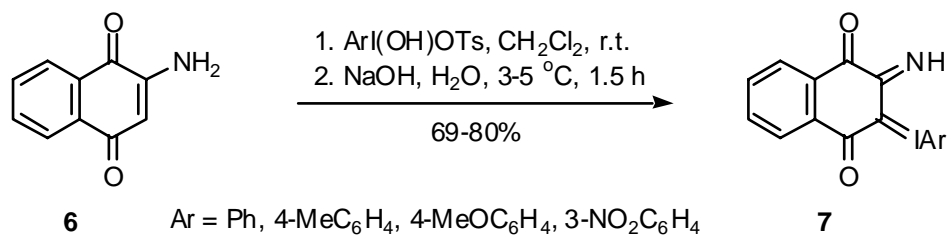
**Synthetic applications of aryl iodine(III) dicarboxylates.** In his pioneering research, Professor Varvoglis and co-workers developed a variety of useful synthetic procedures based on [bis(trifluoroacetoxy)iodo]benzene (BTI) and other aryl iodine(III) dicarboxylates.<sup>11-25</sup> In the early works published in the 1970's and 80's, BTI was applied as powerful dehydrogenating reagent,<sup>11</sup> as a reagent for the oxidative cyclization of 1,3- and 1,4-dioximes,<sup>12,18</sup> for oxidative cleavage of benzyl ethers,<sup>13</sup> oxiranes,<sup>14</sup> diazo compounds,<sup>17</sup> and alkenes,<sup>19</sup> for the oxidation of organic sulfides,<sup>22</sup> for oxidative deiodination of alkyl iodides,<sup>20</sup> and for oxidative halogenation of aromatic compound.<sup>15</sup> On the basis of these reactions, several useful synthetic methodologies were developed and applied by numerous research groups. More recently, in 1990's Tassos reported direct  $\alpha$ -acetoxylation of arylacetonitriles with (diacetoxyiodo)benzene (DIB),<sup>24</sup> oxidative cyclization of tryptamine enamines to functionalized tetrahydro- $\beta$ -carboline,<sup>25</sup> and preparation of spirocyclohexadienones by the reaction of phenolic enaminone derivatives with hypervalent iodine reagents.<sup>26</sup> He has also investigated reactions of BTI and DIB with phenol ethers and some other substrates leading to new iodonium salts and ylides.<sup>27-29</sup> In a series of collaborative papers of Tassos, DIB, BTI, and [hydroxy(tosyloxy)iodo]benzene were used as efficient photoinitiators for the polymerization of methacrylate derivatives and other olefinic monomers.<sup>30-35</sup>

**Preparation of new classes of hypervalent iodine compounds.** Professor Varvoglis and co-workers have first reported the preparation of novel, stable hypervalent iodine compounds with I-N and I-S bonds (structures **1-3**).<sup>36-40</sup> The bisimidates **1** and **2** act as mild oxidizing reagent; compound **2** can be used for functionalization of ketones at  $\alpha$ -carbon to the respective saccharinyl derivatives.<sup>36,38</sup> New, synthetically useful reagents **4** and **5** were also prepared and their chemistry was investigated.<sup>41,42</sup> Reagent **5** is especially useful for the direct  $\alpha$ -(10-camphorsulfonyl)oxylation of various ketones and carbonyl compounds with an active methylene group.<sup>42</sup>

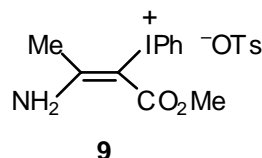
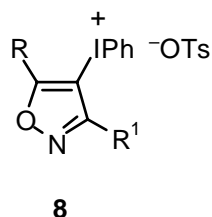


Tassos and co-workers have also reported experimental evidence toward the formation of several novel unstable hypervalent iodine derivatives, such as, phenyliodine(III) diphenolates,<sup>42</sup> and trifluoroethylidonium salts from cyclic enaminones.<sup>44</sup>

**Preparation and chemistry of new ylides and zwitterionic iodonium compounds.** The chemistry of iodonium zwitterionic compounds has been the major area of interest of Professor Varvoglis.<sup>45-59</sup> He and his co-workers have first reported the synthesis and reactivity of phenyliodonium bis(phenylsulfonyl)methylide,  $\text{PhIC}(\text{SO}_2\text{Ph})_2$ .<sup>46</sup> This and the similar sulfonyl-stabilized iodonium ylides have demonstrated a rich and synthetically useful chemistry, including cycloaddition reactions, C–H bond insertion, and tranzylation on sulfur, nitrogen, and phosphorus nucleophiles.<sup>46,49,50-54,56</sup> Tassos and co-workers have also prepared and investigated various zwitterionic iodonium compounds derived from substituted benzoquinones.<sup>48,55,57-59</sup> A recent example of these compounds is shown in a scheme below. A new class of stable zwitterionic arylidonium compounds **7** was prepared from 2-amino-1,4-naphthoquinone **6** and [hydroxy(tosyloxy)iodo]arenes. Ylides **7** show an interesting reactivity: upon heating, aryl migration from iodine to nitrogen is observed, while the photochemical reaction with aromatic compounds and furan leads to substitution products. Nucleophilic attack of sodium alkoxide derivatives on these zwitterions results in opening of the quinone ring affording synthetically interesting multifunctional products.<sup>57-59</sup>



**Chemistry of iodonium salts.** Professor Varvoglis and co-workers have reported the preparation and chemistry of several new iodonium salts.<sup>27,44,60,61</sup> He has first reported cycloaddition reactions of alkynyliodonium tosylates with 1,3-dipoles resulting in novel isoxazolyl(phenyl)iodonium salts **8**.<sup>60</sup> New alkenyl(phenyl)iodonium tosylate **9** was recently prepared from methyl 3-aminocrotonate and [hydroxy(tosyloxy)iodo]benzene. Iodonium salt **9** reacts with various nucleophiles affording substituted enamine derivatives of crotonic acid.<sup>61</sup>



Recently, Tassos and co-workers reported several interesting, new reactions of alkynyliodonium salts with dimedone anion<sup>62</sup> and phenolates,<sup>63</sup> and a reaction of (cyano)phenyliodonium triflate with alkenes.<sup>64</sup>

**Structure and physico-chemical properties of hypervalent iodine compounds.** Professor Varvoglis with co-workers and collaborators published several papers devoted to structural characterization of different classes of hypervalent iodine compounds and their physico-chemical properties.<sup>65-71</sup> In addition, the electrochemical reduction of hypervalent iodine compounds was investigated.<sup>72-75</sup>

Apart from his original publications, Professor Varvoglis contributed five reviews<sup>76-80</sup> and two books,<sup>81,82</sup> all in the area of hypervalent chemistry. His first book,<sup>81</sup> a fundamental monograph covering preparation, structure and chemistry of all structural types of organic polyvalent iodine compounds, is the most comprehensive source of information on the hypervalent iodine chemistry. The second book is a comprehensive monograph on the synthetic applications of hypervalent iodine reagents.<sup>82</sup> Both books have become the most frequently cited references on the chemistry of hypervalent iodine. Also, Tassos is the author of chapters in the multivolume work *Comprehensive Organic Functional Group Transformations*<sup>83</sup> and in the book *Hypervalent Iodine Compounds*, which will appear in early 2003 in the "Topics in Current Chemistry" series published by Springer.

Chemistry plays an important role in non-strictly academic interests of Tassos. Thus, he has published two articles about *Chemistry and Literature* and *The Impact of Mme Curie and Radium in Literature*.<sup>84,85</sup> Currently he is involved in an ambitious work to be titled *the Chemist's Literary Companion*, in which excerpts from many literary works (novels, poems and plays) will be presented. He has already collected material from more than 100 authors, and he will be glad to come in contact with colleagues of similar interests.

Tassos has written several books dealing with organic chemistry at various levels, in Greek, to be used by his students. Also, he has published five books popularizing chemistry, with the following titles: *A Distillate of Chemistry*, *The Secret Charm of Chemistry*, *Portraits of the Chemical Elements* and two volumes with short biographies of noted chemists, from Lavoisier to Pauling. A book of a different kind was his photographic album with ironworks from Greece. This is his main hobby outside chemistry and he already possesses a rich collection of photos (balconies, iron gates, etc) from all over the world.

Tassos is married to Adamantia (Toula), a retired pharmacist, and they have two daughters: the elder, Lisa, is a psychologist, who works in Athens, whereas the younger, Aliki, is a lecturer in American Literature at the University of Dundee. Aliki co-authored the two papers dealing with literary aspects of chemistry.

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