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Recent advances in sulfur- and phosphorous-centered radical reactions for the formation of S–C and P–C bonds

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1. Introduction

Free radicals are important subjects in organic, bioorganic, medicinal, material, and atmospheric chemistries. Synthetic utilities of free radicals have been well-accomplished in polymer chemistry. Even it still has limited applications in the large-scale synthesis of pharmaceutical and agricultural chemicals, synthetic free radicals have attracted extensive attention from the organic community in last several decades.[1,2] Significant progresses have been made in the development of new methods for the generation of carbon- and heteroatom-centered radicals, for better understanding of their physical and chemical properties, and for their synthetic applications. Different from ionic and metal-catalyzed reactions, free radical reactions have unique features such as mild reaction conditions, good functional group tolerance, predictable reaction processes, a broad selection of solvents, and multiple ways for the generation of radicals (Fig. 1).[3] Free radical transformations such as cyclizations,[4] cascade/tandem/domino reactions,[5] fragmentations,[6] atom and group transformations,[7] hydrogen abstractions,[8] and ring expansion reactions[9] are difficult to be replaced by non-radical reaction processes. A wide range of free radical reactions have been developed for the synthesis of complex molecules and natural product analogs[10] by addressing stereoselective[11] and enantioselective[12] issues. Major progress has been made to conduct free radical reactions under environmental benign conditions[13] using tin-free reagents,[14] using photolysis to promote the reactions,[15] using water as a solvent,[16] and using microwave as a heating source.[17] In addition to carbon-centered radicals, the synthetic utilities of heteroatom-centered radicals such as oxygen,[18] nitrogen,[19] sulfur,[20] phosphorous,[21] silicon,[22] and selenium[23] have received increased attention.

There are a number of excellent reviews and book chapters on sulfur-centered radicals[16b,20] and phosphorous-centered radicals[21] that have been published in last two decades. This article covers papers published from 2000 to 2014. The scope is limited to the

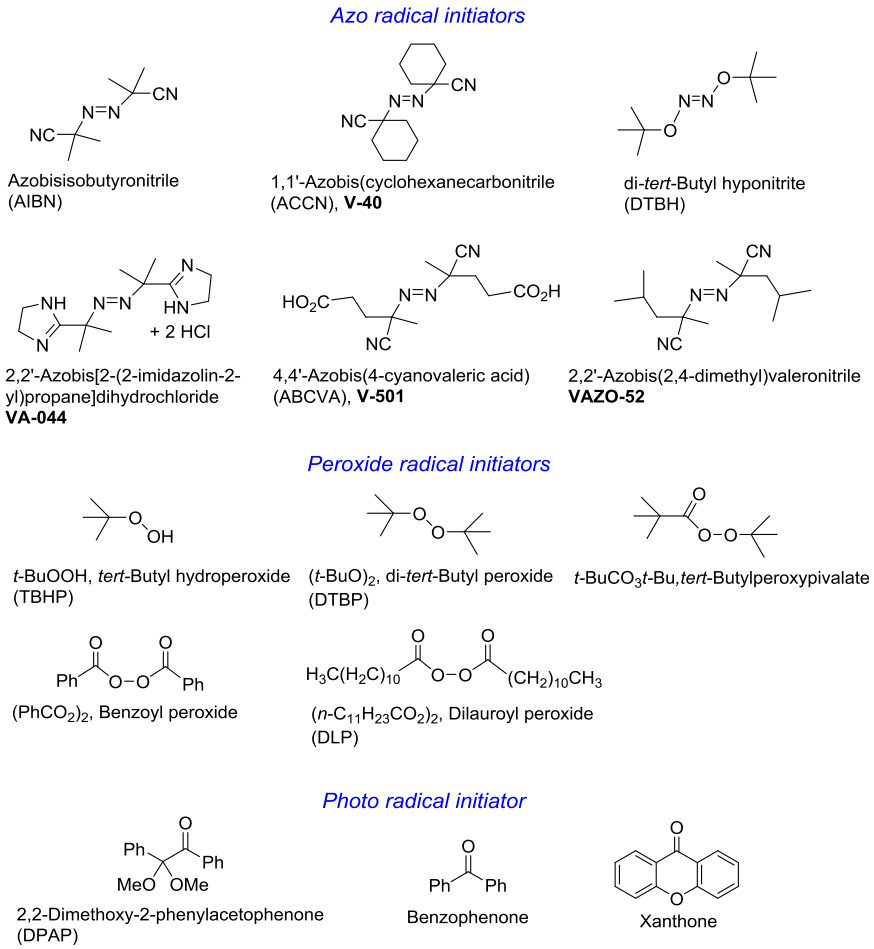

Fig. 1. Representative radical initiators.