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Oxidopyrylium [5+2] cycloaddition chemistry: Historical perspective and recent advances (2008–2018)

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ABSTRACT

The following review article provides an overview of oxidopyrylium [5+2] cycloaddition chemistry, with a particular emphasis placed on seminal historical developments and advancements made over the last decade. It is our hope this review serves as a valuable resource to those interested in the oxidopyrylium cycloaddition chemistry, and helps inspire future advancements.

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1. Introduction

Oxidopyrylium cycloaddition chemistry allows rapid access to often stereochemically dense bicyclic scaffolds, and has found a powerful, established role in the synthetic organic chemistry community (Scheme 1). Given this value, reviews covering various aspects of oxidopyrylium cycloaddition chemistry can be found throughout the recent synthetic organic chemistry literature. However, for the most part these reviews are only specific to a given class of oxidopyrylium cycloaddition chemistry,¹ or are reviewed within a broader context.²

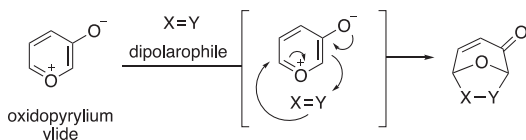
The last review devoted solely to oxidopyrylium cycloaddition chemistry was published in this journal in 2008 by Singh and Trivedi.³ Since then, substantial new developments have been made, including new methods for generating oxidopyrylium ylides and some of the first asymmetric catalytic variants of the reaction. Thus, we felt that an updated review attempting to cover all advancements of the last decade was warranted. In addition, as the prior review was not an exhaustive review covering all strategies available for oxidopyrylium cycloaddition chemistry, we have also attempted to provide a more thorough resource that touches on every general strategy towards oxidopyrylium ylides we have become aware of in our research. It is our hope that this review will serve as a valuable resource to those interested in oxidopyrylium cycloaddition chemistry, and help inspire new developments and advancements in the area.

2. Early methods for entry into oxidopyrylium ylides

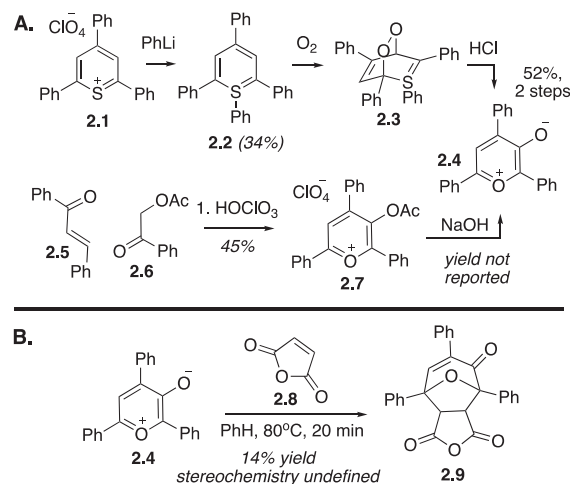
2.1. Synthesis and cycloaddition reactivity of 2,4,6-triphenyloxidopyrylium ylide

The earliest manuscript detailing the synthesis of an oxidopyrylium ylide came from the lab of Charles Price in 1961, who was studying the reactivity of a newly described thiopyrylium species.⁴ Following treatment with phenyl lithium, one of these compounds (**2.1**, Scheme 2A) led to new thiopyrans that reacted rapidly under an oxygen atmosphere to form an unstable cyclic peroxide (**2.3**). When treated to gaseous HCl, the peroxides underwent rearrangement and thiophenol elimination to create 2,4,6-triphenyl oxidopyrylium ylide (**2.4**). To assist in structural confirmation, the ylide was also synthesized using condensation chemistry (**2.5** + **2.6** → **2.4**). One year later, the group disclosed their findings that the oxidopyrylium species could react with maleic anhydride to afford [5+2] cycloaddition products (Scheme 2B).⁵

Since these seminal studies, only a few publications have emerged that highlight the synthetic utility of the 2,4,6-



Scheme 1. Cycloaddition of an oxidopyrylium ylide.

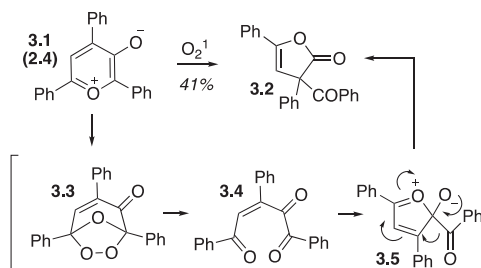


Scheme 2. (A) Synthesis of triphenyloxidopyrylium ylide (Price, 1961) and (B) reactivity with maleic anhydride (Price, 1962).

triphenyloxidopyrylium ylide. For example, in 1970, Wasserman found that the molecule reacted with singlet oxygen to form butenolides (**3.2**, Scheme 3). It was proposed that the first step of the mechanism is a [5+2] cycloaddition between the oxidopyrylium ylide and oxygen (**3.1** → **3.3**, Scheme 3).⁶

By far the most thorough substrate scope study on oxidopyrylium [5+2] cycloadditions with 2,4,6-triphenyloxidopyrylium ylide was carried out by Potts in 1972.⁷ Several oxabicyclic products could be generated through this strategy (Scheme 4), which emphasized how the oxidopyrylium species could react with a broad range of dipolarophiles including electronically poor **4.3**, electronically rich **4.5**, and strained alkenes **4.4**. 2,3-Diphenylcyclopropenethione underwent the cycloaddition as well, giving rise to formal 5C + 3C product **4.6**.⁸ Finally, phenyl isocyanate also worked in the cycloaddition, providing thiolactam **4.7**. These studies demonstrated the versatile nature and general cycloaddition reactivity of oxidopyrylium ylides.

Finally, in 1983, Friedrichsen showed that 6,6-Diphenylfulvene



Scheme 3. Formation of **3.2** between 2,4,6-triphenyloxidopyrylium ylide and singlet oxygen (Wasserman, 1971).

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