

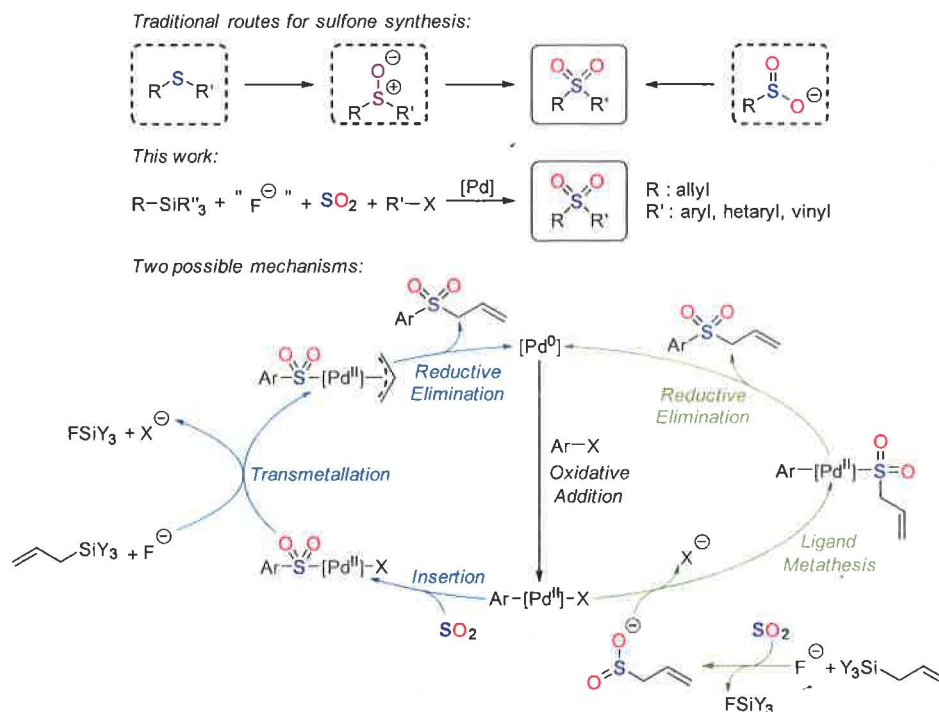
SO₂ Conversion to Sulfones: Development and Mechanistic Insights of a Sulfonylative Hiyama Cross-Coupling Reaction

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Due to distinctive structural and electronic features, sulfones have attracted a particular attention over the past few decades, making it a widespread functional group.¹ Present in many contemporary pharmaceuticals and agrochemicals, they are also used as essential intermediates in organic synthesis. Therefore, numerous methodologies have been developed for their preparation.¹ However, the most common methods (see Scheme below) suffer from significant limitations with harsh reaction conditions or regioselectivity issues. Recently, the insertion of a molecule of sulfur dioxide between two partners was investigated and reactions involving organomagnesium,^{2a} organozinc^{2b} and organoboron^{2c} compounds were reported. As regards the use of organosilanes to produce sulfones from SO₂ or SO₂ surrogates, developed routes are limited to the formation of an intermediate sulfinate anion that undergoes S-alkylation and therefore to sp³-hybridized electrophiles only.³ Herein we report the first Hiyama cross-coupling, enabling the synthesis of sulfones in a direct single-step from organosilanes, SO₂ and sp²-hybridized electrophiles. Different mechanistic pathways were envisaged and discussed both from an experimental and theoretical standpoint.



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