

Organophosphorus and organosulfur chemistry

Reading Lecture course: *Heteroatoms in Organic Synthesis*, Prof. D. M. Hodgson
 G. H. Whitham, *Organosulfur Chemistry*, Oxford Chemistry Primer #33
 J. Clayden, N. Greeves & S. Warren, *Organic Chemistry*, Chapters 31 & 46
 J. I. G. Cadogan, *Organophosphorus Reagents in Organic Synthesis*

Topics for notes*Phosphorus*

Oxidation states: P(III) vs. P(V); Nucleophilicity of phosphines; P=O (or P=S) bond formation as a driving force; Ylids in olefination reactions (including rationalisation of diastereoselectivities)

Staudinger reaction; Wittig reaction; Wadsworth–Emmons reaction; Schlosser modification; Still–Gennari modification; Perkov reaction; Arbusov reaction; Corey–Winter reaction; Mitsunobu reaction; Vilsmeier formylation; Corey–Fuchs reaction; Barton alkene synthesis

Sulfur (and Selenium)

Redox chemistry (sulfides, sulfoxides, sulfones); Nucleophilicity of sulfides (inc. neighbouring group participation); Sulfonate esters as leaving groups; α -Anion chemistry; Sulfur ylids; Dithianes (use as acyl anion equivalents/hydrolysis/Mozingo reduction); [2,3]-Sigmatropic rearrangement of allyl sulfoxides; Pyrolytic elimination reactions; Radical deoxygenations (Barton–McCombie; Barton's PTOC Esters); Lawesson's reagent; SeO₂ as an oxidant (e.g., allylic oxidation)

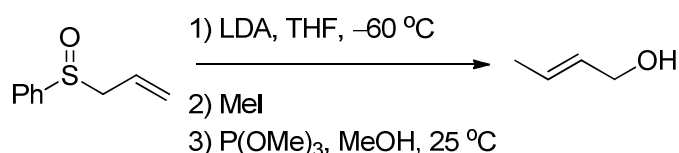
Ramberg–Bäcklund reaction; Julia olefination and variants; Pummerer rearrangement; Swern/Moffat oxidations; Shapiro reaction; Eschenmoser's sulfide contraction; Stevens rearrangement; Sommet–Hauser rearrangement; Riley reaction

Tutorial Problems

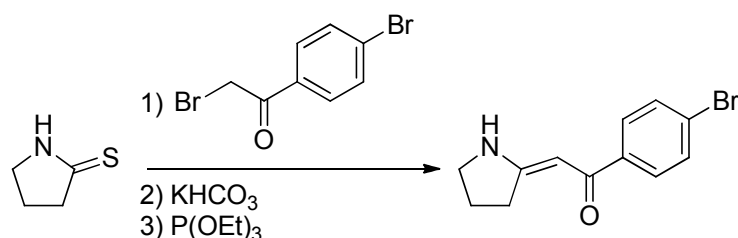
Provide mechanisms and full explanations for the following, providing structures for products where not shown, and commenting on aspects of regio- and stereoselectivity where relevant.

Phosphorus

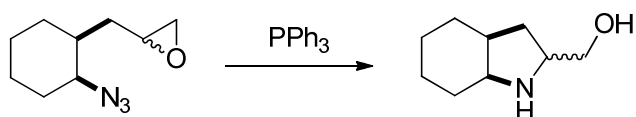
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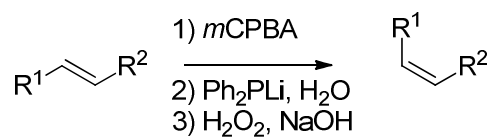
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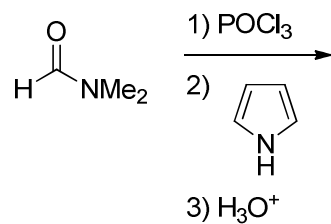
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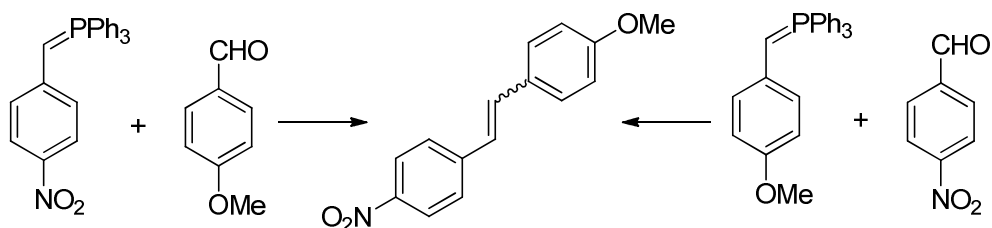
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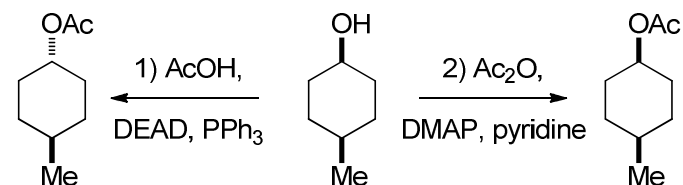
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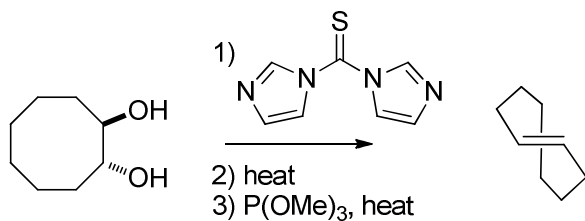
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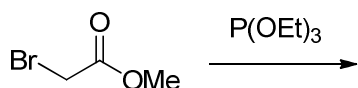
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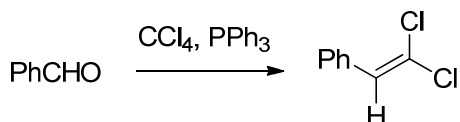
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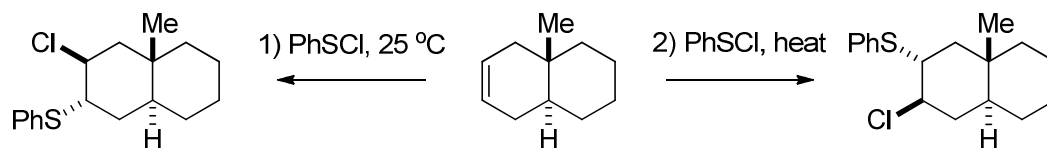


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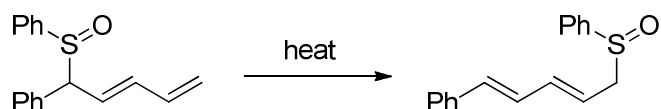


Sulfur

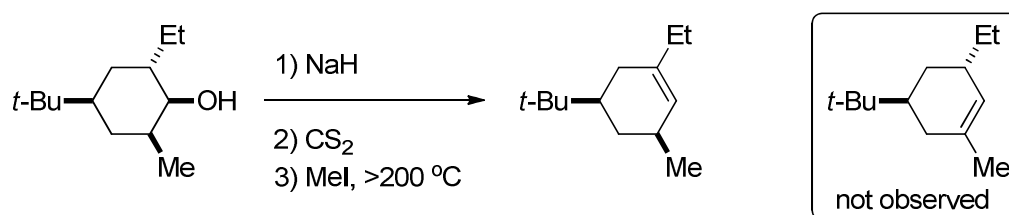
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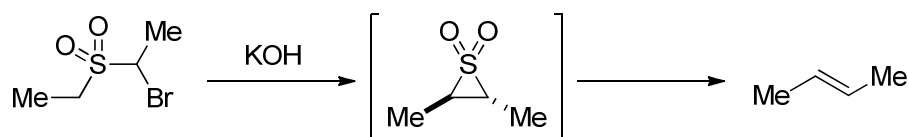
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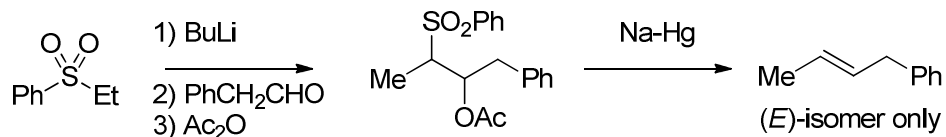
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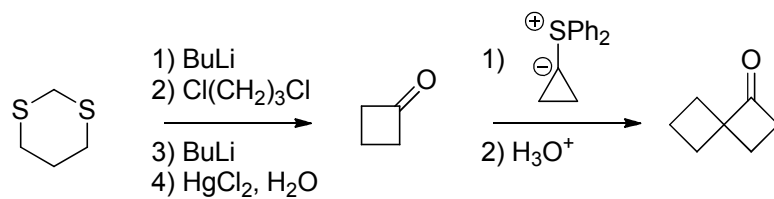
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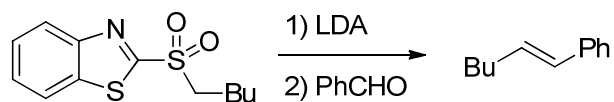
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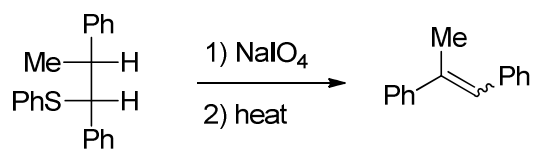
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