Prof D Craig **Organic Synthesis** **Lecture 6** 18.10.02

CARBANIONS STABILISED BY SECOND-ROW ELEMENTS [continued]

Sulfoxides

Sulfoxides have an extra oxygen atom attached to the sulfur atom: it's not surprising, therefore, that it's much easier to remove protons □- to the sulfoxide group than in the less electron-withdrawing sulfide. Typical conditions for this reaction are LDA in THF at -78°C. The resulting carbanionic species react with electrophiles as do sulfide-derived carbanions, i.e. they may be alkylated by reaction with haloalkanes (usually iodoalkanes), and hydroxyalkylated by reaction with carbonyl compounds. Sulfoxides have an added attractive feature: if the two groups attached to sulfur are different, the sulfur atom is asymmetric, and the sulfoxide is chiral. This may induce asymmetry in newly-formed stereocentres, making sulfoxides useful reagents in asymmetric synthesis.

Sulfones

These are the most highly oxidised members of the group of organosulfur compounds we've been looking at. Again not surprisingly, it's still easier to deprotonate □- to the sulfur atom: *n*-BuLi/THF/-78°C is a common set of reaction conditions. The anion solutions are often yellow in colour; the anions react well with haloalkanes, carbonyl compounds, and even epoxides and aziridines, though higher temperatures are required for the latter types of electrophile. The products of the reactions with aldehydes are anions of □-hydroxysulfones, which may be reacted in situ with electrophiles such as benzoyl chloride. Reductive elimination of these intermediates with sodium amalgam, or **samarium(II) iodide** then gives alkenes: this is the basis of the **Julia olefination reaction** (Prof. Marc Julia, École Normale Supérieure, Paris; Ph.D. Imperial College, 1948). It's complementary to the Wittig reaction (see below), in that the products are predominantly *trans*-alkenes.

Sulfur ylides (not strictly carbanions)

Sulfonium ylides, or sulfuranes may be used in the synthesis of epoxides. Deprotonation □- to the R_2S^+ group gives the ylide, which adds into the carbonyl compound. The resulting reactive intermediate extrudes dimethyl sulfide to give the epoxide.

Phosphorus-stabilised carbanions

You are all familiar (I hope) with the **Wittig** (Nobel Prize, 1979) reaction, in which a phosphonium ylide, or phosphorane (again, not strictly a carbanion) reacts with a carbonyl compound (it works best with aldehydes) to give an alkene, together with triphenylphosphine oxide. The stereochemistry of the new double bond varies according to the nature of the phosphorane. It's a great reaction, but the triphenylphosphine oxide can be a nuisance to get rid of. An attractive alternative is the **Wadsworth-Emmons** reaction, in which anio
(not ylides) stabilised by phosphonates react with aldehydes. The by-product is now wate
soluble dialkyl phosphate; the stereochemistry of the new double bond is mostly tran
Phosphonates with heteroatomic □- substituents are useful for making more high
functionalised alkenes.