

Additive Pummerer Rearrangements. Asymmetric Synthesis of (–)-Methyl Jasmonate

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Examples of mild, additive Pummerer rearrangements are given; one example involves asymmetric carbon–carbon bond formation as the key step for synthesis of (–)-methyl jasmonate.

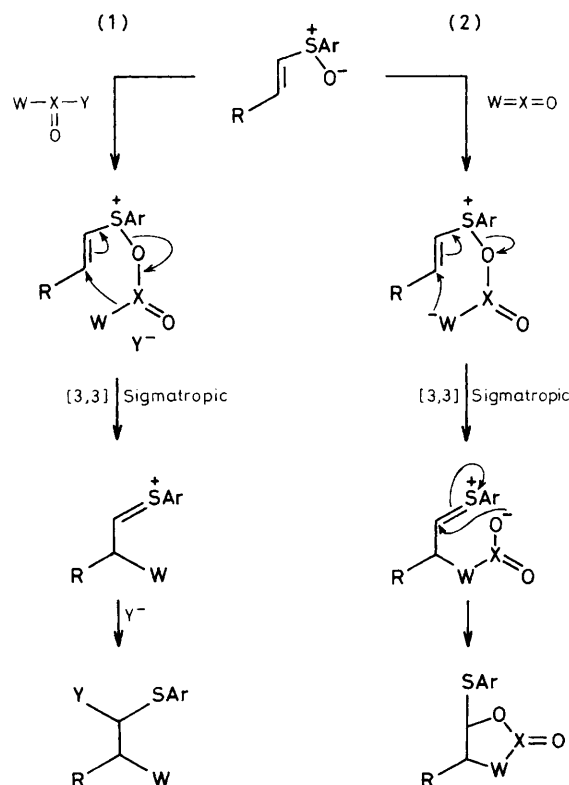
There are relatively few examples of additive Pummerer rearrangements involving direct conversion of α,β -unsaturated sulfoxides into α,β -disubstituted sulphides.¹ Scheme 1 represents two general pathways for such additive Pummerer rearrangements; we report here specific examples of each pathway as well as the application of pathway 2 to an asymmetric synthesis of (–)-methyl jasmonate, an important perfume essence.²

Alk-1-enyl phenyl sulfoxides (1)³ were treated with 5 equivalents of thionyl chloride⁴ in methylene chloride at –5 to +25 °C for 30 min to produce α,β -dichlorosulphides† (2) in 85–95% yield (equation 3); this transformation is an example of pathway 1 in Scheme 1.

Illustrating pathway 2, enantiomerically pure cyclopentenone sulfoxide (3)⁵ was treated with dichloroketene (generated *in situ* from dichloroacetyl chloride and triethylamine)⁶ in diethyl ether at reflux for 15 min to form α,β -disubstituted sulphide (4).† This is the first example of an asymmetric⁷ additive Pummerer rearrangement involving a carbon–carbon bond forming step, and it might also be considered to involve a [3,3] sigmatropic rearrangement of a doubly charged intermediate (see Scheme 1).⁸ Reductive opening of the lactone ring⁹ and esterification gave β -ketosulphide (5) which was C-alkylated and desulphurized to produce (–)-methyl jasmonate (6), [α]_D = –18°, in ca. 20% enantiomeric purity,¹⁰ which was spectroscopically identical to an authentic sample of (±)-methyl jasmonate (equation 4).

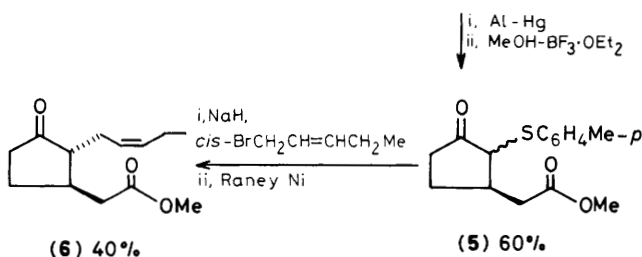
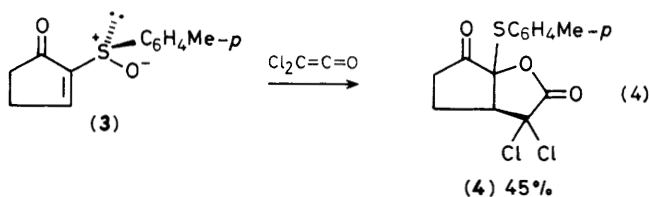
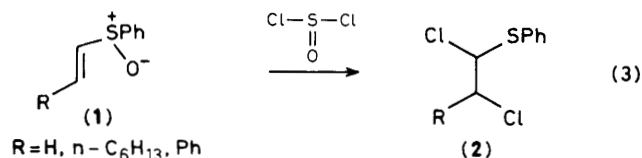
The transformations shown in equations 3 and 4 represent mild and potentially useful reactions which further expand the synthetic utility of α,β -unsaturated sulfoxides.^{11,12}

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Scheme 1

† All new compounds were fully characterized spectroscopically and, when sufficiently stable, analytically.



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