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 sulphoxides 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 sulphoxides (**1**)[3] were treated with 5 equivalents of thionyl chloride[4] 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 sulphoxide (**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 asymmetric[7] 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 ring[9] and esterification gave β-ketosulphide (**5**) which was *C*-alkylated and desulphurized to produce (−)-methyl jasmonate (**6**), $[\alpha]_D = -18°$, 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 sulphoxides.[11,12]

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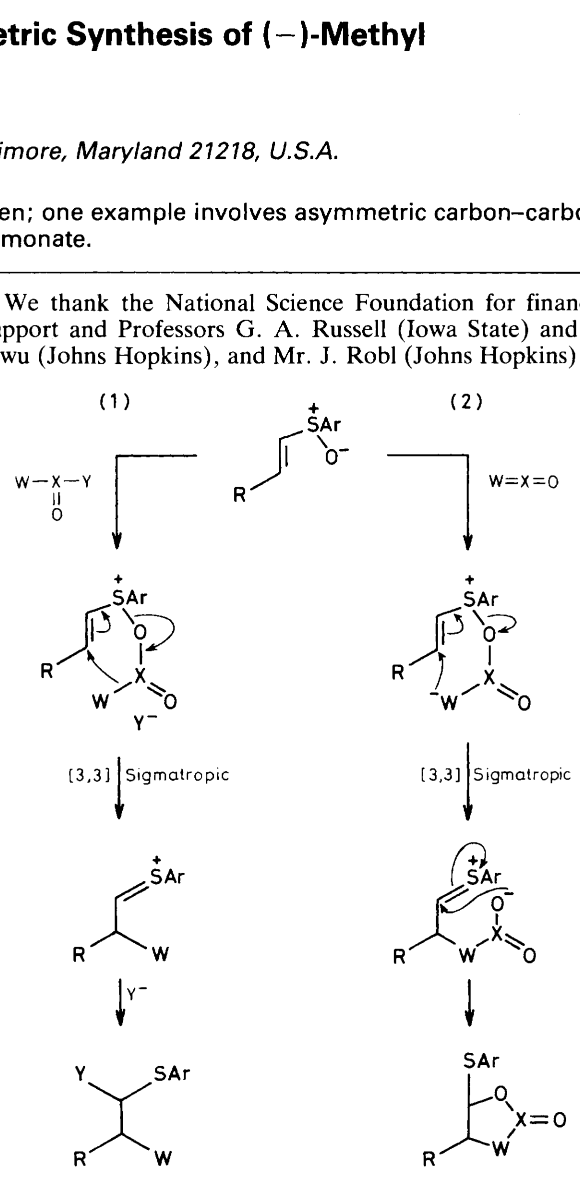
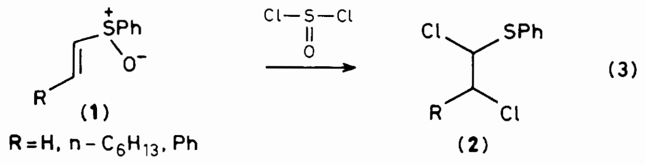
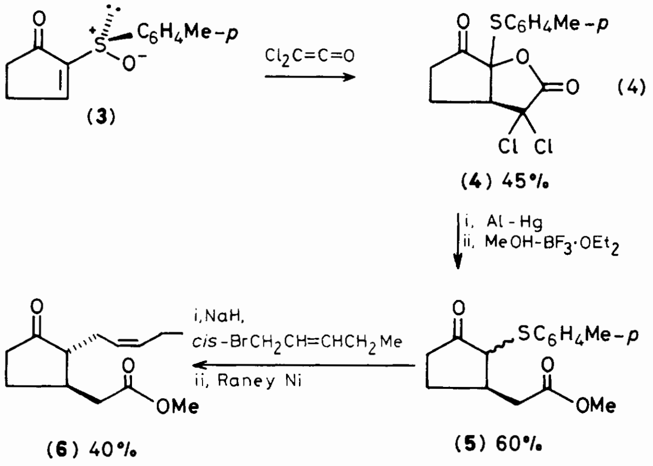


Scheme 1

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





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